INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The One Hundred and Twentieth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday, May 14, 1929, Dr. A. E. Dunstan, President, in the Chair.

The Secretary announced that the following had been elected :—

Members.—Ronald Devereux Carty, John Alexander McKinlay, Lionel James Truss, Joseph Horace Vine, Cary Richard Wagner.

Transference to Member.—William Eric Frankenburg, Lew Suverkrop, George Herbert Willock.

Associate Members.—Cyril George Cooper, Geoffrey Annesley Ferrar Grindle, William Raymund Young.

Associate.—Cecil Bernard Dow Fox.

The President announced that the present meeting was the last of the Session and that the next meeting would be held on October 8, when a symposium on the question of gum formation in motor fuel would take place, the first paper being by Dr. S. J. M. Auld. It was hoped to obtain a number of papers dealing with the topic in order that there might be a thorough discussion of the whole problem. He further desired to announce that the Institution's handbook on Standard Tests was in the press and was expected to be issued in about fourteen days' time.

Very unfortunately one of the authors of the papers about to be read—Dr. Wheeler—was lying sick in Sheffield, but he desired cordially to welcome Dr. Wheeler's late associate and joint author of the papers about to be read, Dr. Maxwell. Dr. Maxwell would describe a continuation of the most important researches inaugurated in Sheffield and detailed at a meeting of the Institution held a year ago, at which for the first time an account was given of the very extraordinary afterglow or after-burning effect that was correlated with the phenomenon of pinking in internal-combustion engines.

The following papers were then read by Mr. Maxwell :—

Flame Characteristics of "Pinking" and "Non-Pinking" Fuels. Part II.

By G. B. Maxwell and R. V. Wheeler, D.Sc. (Member).

In Part I. of this research* the results of a study of the flames of explosions of mixtures of iso-pentane and air and of benzene and air in a closed horizontal cylinder were recorded. Iso-pentane, a "pinking" fuel, was found under certain conditions to produce effects in the closed cylinder similar to those of a pinking explosion in an engine cylinder, and the same alterations in conditions as are found in practice to reduce or eliminate pinking in the engine cylinder reduced or eliminated the pinking phenomena in the closed cylinder. Records of the development of pressure and of the propagation of flame from one end of the cylinder to the other (recorded simultaneously on a revolving photographic paper) showed that in a pinking explosion the disturbance responsible for the shrill note of the explosion occurred almost at the end of the flame propagation. At the moment when the flame-front (which accelerated and began to vibrate towards the end of its travel) reached the end-plate of the cylinder, a compression-wave travelled back throughout the length of the cylinder and seemed to be maintained by a further release of thermal energy, an intense glow appearing throughout the products. Little or no "after-burning" was evident in the wake of the flame-front as it travelled. On the other hand, with benzene, a non-pinking fuel, combustion was continuous and long-continued behind the flame-front.

These observations have been confirmed and extended by experiments with other fuels and blends of fuels. The apparatus and method of experiment were the same as described in our previous paper (*q.v.*), except that, in order to facilitate the evaporation and mixing of some of the liquid fuels with the air, a small fan was fitted centrally within the cylinder. The fan shaft passed through the centre of one end-plate (that at which ignition was effected) and the fan was drawn back flush with the end-plate before exploding the mixture. This arrangement necessitated placing the sparking-plug otherwise than at the centre of the end-plate, as it was in the previous series of experiments. It was placed one inch vertically below the centre. This disposition of the point of ignition slightly

* J. Inst. Petr. Techn., 1928, 14, 175.

modified the movement of the flame during its early stages, but did not affect the general character of the explosions. The internal dimensions of the cylinder are: length 15 in. and diameter 6 in. A glass window, $\frac{3}{4}$ in. wide, extends along the cylinder from within 1 in. of the ignition end. The flame of each explosion was photographed through this window on rapidly revolving photographic paper, which received also the trace of an optical pressure indicator. When studying the records here reproduced (negatives), the flame can be considered as moving from the bottom to the top of the paper, itself moving from left to right. Actually, the cylinder was horizontal. Opposite to one of each group of three photographs a diagram of the window in the cylinder has been drawn, strengthening bands which obscure it at two places being shown in black.

I. Experiments with Pentane and Benzene.

(*a*) *The Effect of Increased Initial Temperature.*—For all the experiments previously recorded the initial temperature was 15-17° C. For the experiments now to be described, the cylinder was enclosed in a lagged wooden box which could be raised to the desired temperature by electric heater lamps. A sliding shutter in the side of the box in front of the window of the cylinder was withdrawn immediately before firing.

Pentane-Air Mixtures.—When the initial density of the mixtures of pentane and air, and their degree of saturation with water-vapour, were kept constant, progressive increase in the initial temperature up to 100° C. slightly widened the range of mixtures in which pinking occurred. The density employed corresponded to not less than that at 2 atm. at 15° C. The "pink" did not appear to be appreciably louder than at 15° C. and the displacement of the manometer diaphragm was not more violent.

Benzene-Air Mixtures.—At 15° C. and 2 atm. initial temperature and pressure, no mixture of benzene and air was found to give a pinking explosion. When, however, the density being kept constant, the intial temperature was raised above 30° C., a narrow range of mixtures (3·1 to 3·8 per cent. benzene) was found to give faintly audible explosions. As at lower initial temperatures, combustion was continuous behind the flame-front, but the flame accelerated towards the end of its travel and vibrations appeared on the manometer record (see Fig. 1). As with pentane, the range of mixtures giving an audible explosion was slightly widened as the initial temperature was raised up to 100° C. With the initial temperature 100° C. a shock-wave (as indicated by the pressure-record) was sometimes observed. This usually occurred some time

after the initial flame had reached the end-plate of the cylinder, whereas with pentane-air mixtures the two events were always simultaneous.

These results suggest that in a slightly pinking engine, where the mixture strength varies from stroke to stroke, the pink will be less spasmodic as the initial temperature of the charge is raised. Moreover, if the vibrations observed (see Fig. 1) bear any relation to the "rough running" of an engine, that may be expected to become more marked at higher temperatures.

The effect of increased induction manifold temperature in initiating pinking in an engine could hardly have been anticipated from our experiments, but appears to be established. Thus Ricardo (Empire Motor Fuels Committee Report, 1923–1924), using hexane-air mixtures in a variable compression engine, though unable to measure accurately the temperature differences in the induction manifold, found that the compression ratio could be raised by 0·1 for every 10° C. drop in temperature of the carburettor air-intake passage, from 70° to 30° C.

(*b*) *Mixtures with Air of Blends of Benzene and Pentane.*—Blends of benzene and pentane, approximately in the proportions 1 to 3, 1 to 1 and 3 to 1 by volume, were vaporised and mixed with air. The mixtures, each containing about 3·5 per cent. of inflammable vapour, were ignited at 30° C. and 2·1 atm. initial temperature and pressure. The flame photographs, Figs. 1 to 4, show a gradual transition from a typical benzene-air explosion, in which combustion is continuous behind the flame-front, to that of pentane-air, in which the after-burning is suddenly manifested when the accelerated vibrating flame reaches the end of the cylinder.

In these experiments, particularly with mixtures containing equal volumes of pentane and benzene, ignition of the unburnt charge sometimes occurred ahead of the advancing flame. These "auto-ignitions," which always occurred close to the end-plate of the cylinder, produced a second flame which travelled back to meet the original flame at about an equal speed (see Fig. 2). When this occurred, the explosions were not more violent than the normal and the records showed no other unusual feature. Such auto-ignitions would therefore not appear to be a cause of pinking in an engine cylinder.

These experiments confirm the view we have expressed previously, that the main difference between a pinking fuel, such as pentane, and a relatively non-pinking fuel, such as benzene, lies in the nature of the reactions proceeding in the hot gases remaining after the flame has passed. The addition of benzene, the combustion of which is

continuous throughout the explosion, to pentane reduces the likelihood of a pinking explosion by reducing the amount of chemical energy available to maintain a shock-wave when the initial flame is arrested.

(*c*) *The Addition of "Pro-Knocks" to Pentane-Air Mixtures.*—The only two substances which were definitely known to increase the liability to pinking of a straight-run paraffin-base petrol in an internal combustion engine were ethyl ether and amyl nitrite. Experiments were made with these.

Blends of Pentane and Ethyl Ether.—Blends of iso-pentane and ethyl ether, containing approximately 3, 10 and 30 per cent. of the latter by liquid volume, were vapourised and diluted with air to produce mixtures containing about 3·5 per cent. by volume of inflammable vapours. The explosion of such mixtures, at 30° C. and 2·1 atm. initial temperature and pressure, was violent. Comparison of Figs. 4 and 5 shows the effect of ethyl ether in reducing the amount of "after-burning" in the wake of the flame. "Auto-ignition" is apparent in Fig. 5.

Blends of Pentane and Amyl Nitrite.—The addition of small quantities of amyl nitrite vapour (about 0·1 per cent. by volume) to a pinking mixture of pentane and air (3·1 to 3·8 per cent. pentane), initially at 30° C. and 2·1 atm., greatly increased the violence of the pink and decreased the amount of after-burning immediately behind the flame-front (*cf.* Figs. 4 and 6). Of greater interest is the effect of amyl nitrite, in increasing amounts, on the explosion of a normally non-pinking pentane-air mixture. From Figs. 7 to 9 it will be seen that the addition of 0·05 per cent. of amyl nitrite vapour to a 2·8 per cent. pentane-air mixture, the explosion of which by itself (initially at 30° C. and 2·1 atm.) was noiseless, caused the flame to accelerate slightly towards the end of the travel, and slight vibrations appeared on the pressure-record. This explosion gave a slight "ping." The addition of 0·15 per cent. of amyl nitrite vapour (Fig. 9) produced a more violent pinking explosion, with marked reduction in the amount of after-burning behind the flame-front and a correspondingly more intense glow at the moment of pinking. The amyl nitrite has a slight retarding effect on the mean flame speed and on the rate of rise of pressure.

(*d*) *The Addition of Incombustible Gases to Pentane-Air Mixtures.*—Ricardo (*loc. cit.*), as a result of experiments with an aromatic-free petrol in a variable compression engine, found that the addition of cooled exhaust gases or steam raised the H.U.C.R. considerably. We have studied the effect of adding carbon dioxide or steam to mixtures of iso-pentane and air.

The Addition of Carbon Dioxide.—The addition of increasing quantities of carbon dioxide to pentane-air mixtures containing about 3·5 per cent. of pentane progressively reduced the flame speed and diminished the luminosity both of the initial flame and of the after-glow. The explosions were not so loud as with pentane alone, but the pressure oscillations were of considerable amplitude even when as much as 8 per cent. of carbon dioxide was added. The chief effect of the carbon dioxide was to narrow the range of mixtures of pentane and air giving pinking explosions.

The Addition of Steam.—In order to study the effect of steam under constant conditions of temperature and pressure of the pentane-air mixtures, three sets of experiments were made with different mixtures of pentane and air initially at 50° C. and 2·2 atm.: (1) Roughly dried (by passing the mixture through a column of calcium chloride); (2) containing 0·9 per cent. water-vapour; and (3) containing 6·5 per cent. water-vapour (*i.e.*, saturated at 50° C.).

The effect of the water-vapour was most pronounced. The speed of the flame and its luminosity were progressively decreased as more water-vapour was added, and audibility of pinking explosions was greatly reduced and the "after-glow" was nearly eliminated (*cf.* Figs. 10 and 11). Taking into account the heat capacities of carbon dioxide and steam, and assuming that the action of carbon dioxide is solely that of a diluent, it would seem that the action of water-vapour is more than thermal. Ricardo's experiments led him to a similar conclusion.

II. Experiments with Various Fuels.

Explosions of a number of fuels, the behaviour of most of which in an engine cylinder is known, have been studied. As a result it can be said that the flame photographs and pressure-records have, without exception, indicated the same pinking propensities of the fuels as are judged by engine tests. In particular, when the flame photographs show that combustion proceeds continuously behind the flame-front, the fuel is one which does not readily give a pinking explosion in an internal combustion engine. The experiments with some of the fuels have yielded results of particular interest, which are here briefly recorded.

Carbon Disulphide.—One of the difficulties with regard to the explanation of pinking as due to "auto-ignition," is the anti-knock effect of carbon disulphide, which has a low ignition tem-

perature. This difficulty has been largely met by Tizard and Pye (*Phil. Mag.*, 1922 (VI.), 44, 79), who have shown that the lag on ignition of carbon disulphide by compression is abnormally long. The "auto-ignition" of the unburnt portion of the charge by the heating effect of the expanding burning portion can be assumed to be delayed too long for a pink to occur. Our objection to the "auto-ignition" theory is that, when such ignitions occur during an explosion in a closed cylinder (*e.g.*, Figs. 2 and 5), the explosion is no more violent than in their absence. Moreover, what we have termed a "pink" in our cylinder, because it so closely resembles the pink in an engine cylinder, is obtained most commonly without the occurrence of "auto-ignition."

A record of an explosion of a mixture of carbon disulphide and air (8·5 per cent. carbon disulphide), initially at 30° C. and 2·5 atm., is reproduced in Fig. 12. The explosion gave but a faint sound (no other mixture gave the slightest sound on explosion) and it will be seen that the pressure-record shows no sign of vibrations. Combustion was continuous, and long-continued, behind the flame-front.

Hydrogen.—No mixture of hydrogen and air, initially at 15° C. and 2 atm. has been found to produce a pinking explosion similar to those obtained with mixtures of pentane and air. The explosion of some of the richer mixtures gave a slight "click" and the pressure-record then showed slight vibrations. Fig. 13 shows the results obtained with a mixture containing 41·7 per cent. of hydrogen and is typical of rich mixtures. For this photograph the speed of revolution of the camera drum was increased about threefold. It will be seen that the initial flame, the mean speed of which is about ten times as fast as the most rapidly burning pentane-air mixture, has left but a faint impression on the photographic paper (it has been necessary to accentuate the record for reproduction), but fairly intense after-burning has occurred some time before the flame-front reached the end-plate, and an after-glow has travelled back for a short distance from the end-plate at the moment that the flame-front reached it. Thereafter a diffused glow persisted for several centi-seconds. This continued "after-burning" with hydrogen suggests considerable residual energy after the passage of the flame through the cylinder, whilst from the sudden arrest of this rapid flame a marked recoil might be expected. The records show such a recoil, but the pressure-pulse is not maintained, perhaps because the mean temperature and density of the gases, which are low compared with those resulting from the explosion of pentane-air mixtures, are insufficient.

III. Stationary Pressure Waves.

Attention has already been directed to the vibration and acceleration of the flame, accompanied by an increase in the rate of rise of pressure which is considerable when the initial compression is high, in all audible explosions in the closed cylinder. Marked striations appear in the flame photographs of such audible explosions, if they are "analysed" by a sufficiently rapid speed of rotation of the camera drum. Fig. 14, the record of an explosion of a 3·35 per cent. pentane-air mixture, initially at 30° C. and 4 atm., is a typical example. Parallel alternate light and dark bands first appear just behind the flame-front after it has travelled about three-quarters of its full distance. After the flame-front reaches the end-plate, the striations persist for several centi-seconds, extending some distance from each end towards the centre of the cylinder. The after-glow near the centre, though not marked by striations, reveals the existence of pulsations in the gases. The initial vibrations of the manometer diaphragm, which occur simultaneously with the appearance of the flame striations, at first have the same frequency, but, with a pinking explosion, the violent shock to the diaphragm and indicator (which have appreciable inertia) causes vibrations of different frequency, and "beats" occur. These phenomena are exhibited by explosions of mixtures either initially quiescent or rendered turbulent by a rapidly-revolving fan, but with a turbulent mixture a higher initial pressure is required before the striations appear and the explosion becomes audible. A higher initial pressure is required also if the length of the cylinder is reduced from 15 to 9 inches.

The effect of change of length of cylinder on the period of the vibrations, the appearance of the records and the effect of variations in initial pressure to density ratios support the view that the striations are due to the establishment of a stationary longitudinal wave in the column of gases. The initiation of such a stationary wave may possibly be due to the compounding of reflected progressive pressure waves, of the same period and amplitude, such as those recorded by Payman (Proc. Roy. Soc., 1928, 120A, 90) as occurring in the hot products behind a flame in a closed vessel. The striations do not occur solely in records of pinking explosions, such as indicate the passage of a maintained shock-wave, but are noticeable also in comparatively quiet explosions, *e.g.* of acetaldehyde and air (Fig. 15).

Conclusions.

These experiments, and those described in Part I. lead to the conclusion that for a "pinking" explosion to occur in a closed vessel two conditions are necessary: (1) The shape and size of

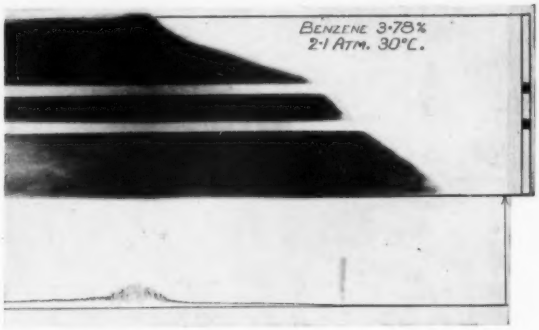


FIG. 1.

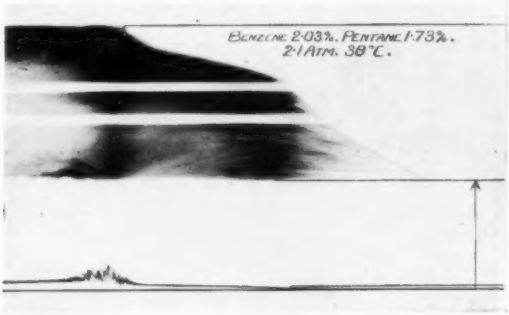


FIG. 2.

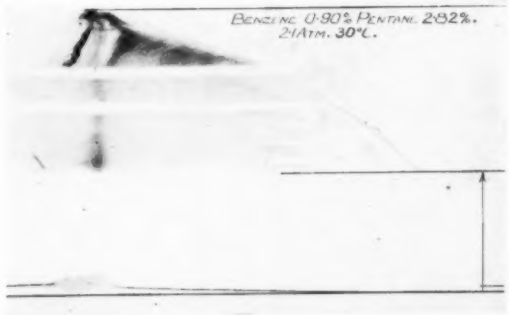


FIG. 3.

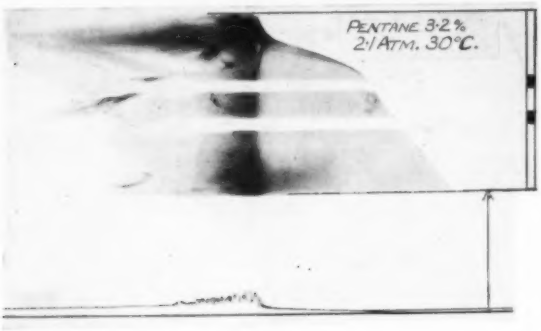


FIG. 4.

FIG. 5.

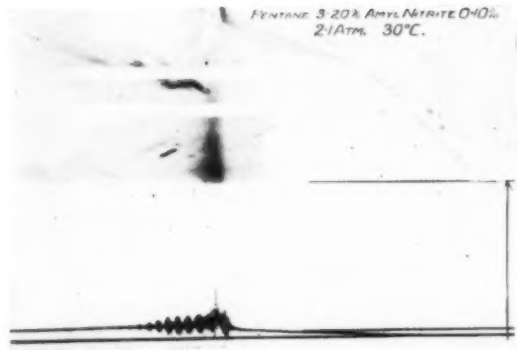


FIG. 6.

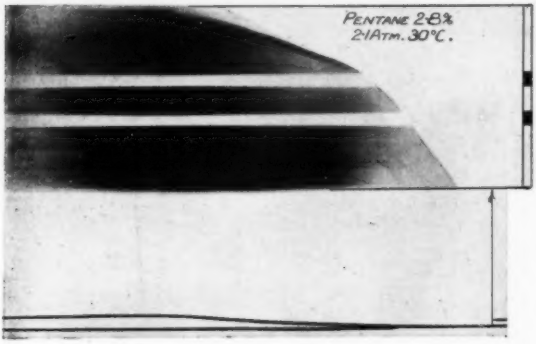


FIG. 7.

FIG. 8.

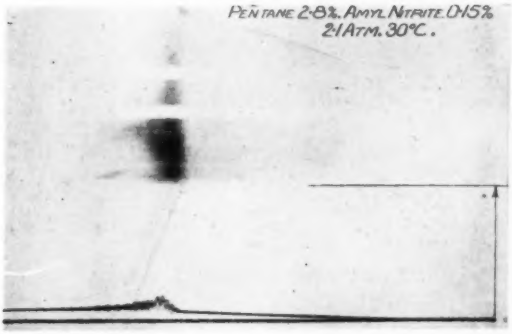


FIG. 9.

FIG. 10.

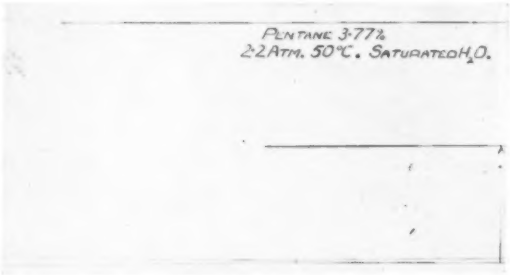


FIG. 11.

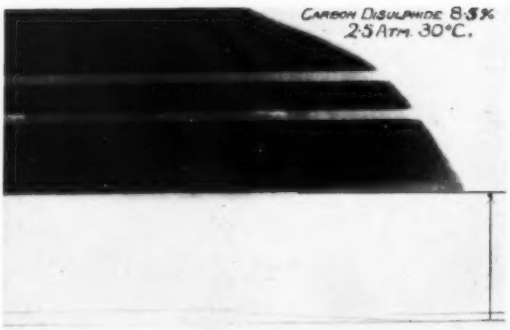


FIG. 12.

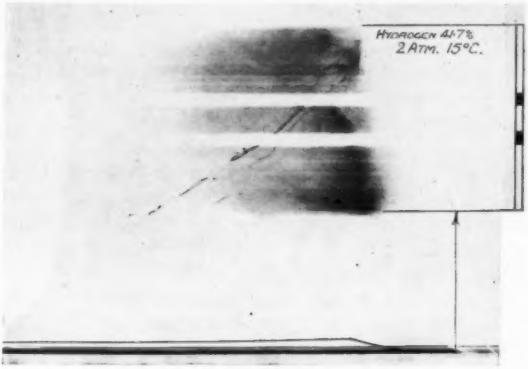


FIG. 13.

FIG. 14.

FIG. 15.

the vessel, the nature and strength of the mixture, and the magnitude and rate of heat liberation in the burning gases must be such that a stationary wave can be set up in the column of gases before the initial flame has travelled throughout the vessel. (2) The nature of the fuel and its concentration in the mixture must be such that there is sufficient residual energy available to maintain a shock-wave when the flame, accelerated by the stationary wave, is arrested by the wall of the vessel.

On these assumptions, the effect of the addition to pentane of traces of "anti-knocks," such as lead tetraethyl, which renders the combustion continuous behind the flame-front, is understandable. Fuels like benzene and carbon disulphide, which themselves burn continuously during explosion, act in a similar manner to lead tetraethyl but less effectively.

The effect of turbulence is probably twofold. It tends to prevent the formation of a stationary wave and it accelerates the combustion in the wake of the flame.

Department of Fuel Technology,
Sheffield University.

The Influence of Cylinder Design on Pinking.

By G. B. Maxwell and R. V. Wheeler.

In previous papers ("Flame Characteristics of Pinking and Non-Pinking Fuels, Parts I. and II.") the suggestion has been made that a pinking explosion in an internal combustion engine is due to the initiation of a stationary pressure-wave in the burnt and burning gases, followed by a maintained shock-wave when the accelerated, vibrating flame impinges on the wall of the combustion-space. The nature of the fuel and its concentration in the charge determine the amount of residual energy available to maintain a shock-wave when the recoil takes place.

There should thus be two principal ways of eliminating "pink": (1) As regards the fuel, its continuous uniform combustion could be encouraged so that little residual energy is available to maintain a shock-wave. For this purpose the admixture with petrol of a fuel, such as benzene, the combustion of which is continuous during explosion, is helpful; or, more effectively, combustion promoters, such as the products of thermal decomposition of lead tetraethyl, can be used. (2) As regards the cylinder, the shape and size of the

combustion-space, and arrangements for providing turbulence, could be so designed as to prevent the initiation of a stationary wave. The present paper describes experiments made to determine how the initiation of a stationary wave can be prevented. The apparatus used for the experiments was essentially the same as that described in previous papers.

The Formation of Stationary Waves in Gaseous Explosions.—The formation of stationary waves in gaseous explosions in closed vessels has been remarked by Egerton and Gates (Proc. Roy. Soc., 1927, **116**A, 516) and others, but the origin of the waves is obscure. Dr. W. A. Kirkby (private communication) has found that the resonance properties of the column of burnt gases behind the flame-front form a determining factor; whilst the rate of heat emission at the flame-front, and the nature of the reactions proceeding in the inflamed portion of the charge, appear also to be of importance.

The Inflammation of Turbulent Mixtures.—Turbulence of the charge seems to inhibit the formation of a stationary wave. The reason is not clear. Turbulence does not appear to influence the acoustic properties of the gas, for, given a sufficiently high initial compression of the charge, a stationary wave can be formed in a turbulent explosive mixture in a closed cylinder and its period is identical with that of the wave formed during the explosion of a quiescent mixture in the same cylinder. Further, turbulence enhances both the magnitude and rate of development of pressure, and therefore the rate of heat emission at the flame-front, a condition which might be expected to promote the formation of a stationary wave. Of the factors previously considered as contributory to the formation of the wave, the character of the reactions proceeding behind the flame-front would thus seem to be most affected by turbulence. That the speed of the flame and the magnitude and rate of rise of pressure do not in themselves determine the formation of a stationary wave in an explosion-vessel of given dimensions, is shown by experiments described elsewhere (*loc. cit.*), where it was found that with any fuel the wave forms most readily in mixtures richer than those giving the maximum pressure and the fastest speed of flame on explosion. Moreover, the addition of small quantities of a "pro-knock" to pentane, though reducing the speed of flame on explosion, encouraged the formation of a stationary wave.

The Influence of the Dimensions of the Combustion-Space.—In comparative experiments in which the length of the cylinder (6 inches in diameter) was 15 and 9 inches, it was found that with mixtures of pentane and air a higher initial compression was required in the shorter cylinder to ensure that on explosion (by ignition at

one end of the cylinder) a stationary wave would be set up. This might be due to either or both of two causes : (1) The higher natural frequency of the shorter column of hot gases to be set in vibration ; and (2) the decreased energy available to give rise to the vibrations, for owing to the increased surface to volume ratio of the shorter cylinder, the maximum pressure produced on explosion of a given mixture was lower than when the longer cylinder was used.

As indicating that the rate of cooling of the products of combustion is a more important factor than the length of run of the flame, experiments in which the diameter of the cylinder was reduced to 4 inches (the length being 15 inches) showed that no mixture of pentane and air would produce an audible explosion even with an initial compression of 4 atm. In the narrow cylinder, the natural frequency of the column of gases was lower than in the wider one (so that the energy required to initiate the vibrations would be less), but the ratio surface-volume was considerably greater.

The Influence of the Shape of the Combustion-Space.—The effect of the acoustic properties of the burning gases, as determined by factors other than their temperature, is shown clearly by the results of explosions in vessels of different shapes. In spheres (1·9, 4 and 8 litres capacity) and in a cube (3·4 litres) no mixture of pentane and air gave an audible explosion (ignition being central) with initial compression up to 2 atm., though the explosion pressures and temperatures were considerably higher than in the cylinder (15 × 6 inches). In some early experiments in the 1·9 litre sphere, a slit in the wall (leading to a window through which the flame could be photographed) formed a small "pocket." Explosions of 3·5 per cent. pentane-air mixtures were then faintly audible and pressure-records showed vibrations (*cf.* Fenning, Aer. Res. Comm. Rep. No. 902). With initial pressures of 3 atm. the explosions (central ignition) of all mixtures of pentane and air were still inaudible in the spheres, but the explosion of a 3·5 per cent. mixture in the cube gave a slight sound. With side ignition in the cube (length of side 6 inches), the same mixture, initially at 3 atm. pressure, gave an audible explosion. Comparative experiments were also made, with a 3·5 per cent. pentane-air mixture initially at 15° C. and 1½ atm., ignited (1) at the bottom of the 8-litre sphere (diameter 9·8 inches) and (2) at the end of a cylinder 9 inches long and 6 inches in diameter. Although the length of run of the flame was approximately the same in each experiment, the former explosion was noiseless whilst in the latter a stationary wave was set up.

The Influence of the Position of the Source of Ignition.—It is usually stated that the most effective position for the sparking-plug

in an engine is the centre of the cylinder head. The effectiveness of this position is attributed to the short distance of travel of flame in any direction, but the shape of the flame, the character of the flame-movement, and the degree of cooling by the walls of the combustion-space all differ from those obtaining when ignition is at the side of the combustion-space. The central position of the plug does not give "central" ignition in the sense employed when describing experiments in closed vessels, for ignition is effected at, or very close to, the cylinder head, corresponding with "end" ignition in a short closed cylinder.

On igniting a 3·5 per cent. pentane-air mixture, initially at 1 atm., at various positions in a closed cylinder 15 inches long and of 6 inches internal diameter, it was found that with ignition at the mid-point a stationary wave was set up during the explosion. The distance of travel of flame, from the centre to the far edge of each end-plate, was about 8 inches. With end-ignition in a cylinder of the same diameter but only 9 inches long, the explosion of a 3·5 per cent. pentane-air mixture, initially at 1 atm., was inaudible. With ignition at the centre of the 15-inch cylinder, the pressure ratio (maximum/initial), and therefore the mean temperature, was but little different from that with end-ignition in the same cylinder, and the period of the stationary wave was the same. With end-ignition in the 9-inch cylinder, however, the pressure ratio and the period of the stationary wave were lower.

From these experiments the relative importance of the various factors on which the formation of a stationary wave may be presumed to depend can be gauged.

The most important appears to be the character of the reactions proceeding in the wake of the flame. With a given fuel, the character of the reactions is dependent mainly on the mean flame temperature, but turbulence can modify them as can the addition of traces of a "pro-knock" such as amyl nitrite. An "anti-knock," such as lead tetraethyl, does not seem to affect the establishment of a stationary wave. It affects the maintenance of the subsequent shock-wave.

The acoustic properties of the charge of gaseous mixture, as determined by the size and shape of the combustion space, play a part in affecting the resonance. Here, again, the mean flame temperature has a controlling influence.

It would seem that, for resonance to be induced, a certain minimum temperature must be exceeded at some point or points in the burnt and burning gases, the stationary wave being formed by the compounding, with their reflections from the ends of the cylinder, of such progressive waves (originating behind the flame-front) as have been noted by Payman (Proc. Roy. Soc., 1928, **120A**, 90).

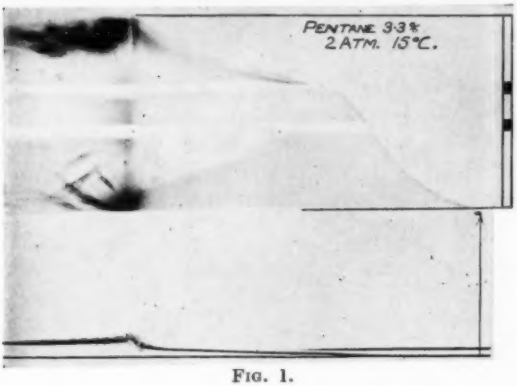


FIG. 1.

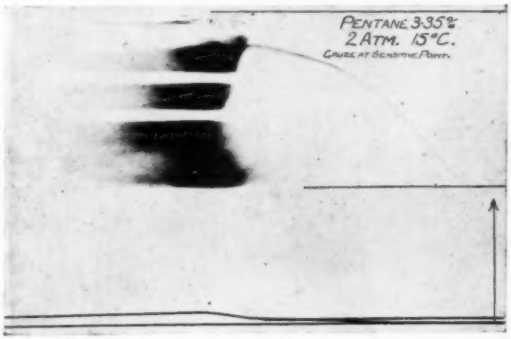


FIG. 2.

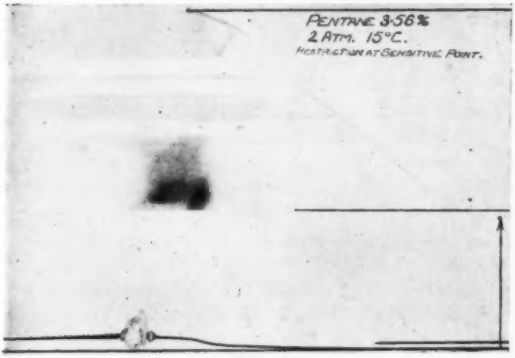


FIG. 3.

These progressive waves appear to be initiated by a sudden disturbance at a point, or at several points, in the wake of the flame.

On this reasoning, the nature of the reflecting surfaces of the cylinder should affect the setting up the stationary wave. The following series of experiments show that this is so.

The Influence of the Contour of the Combustion Space.—Mixtures of pentane and air were ignited at one end of a closed cylinder, 15 inches long and 6 inches in diameter, at constant temperature (15° C.) and various initial pressures, the contour of the far end-plate being varied in different experiments. A concave plate was found to be the most, and a convex plate the least, effective in preventing the formation of a stationary wave. The differences were not so great, however, as to suggest that any marked improvement in engine performance might be expected from designing the cylinder of an engine in accordance with the results obtained in a closed cylinder.

The experiments were extended to the use of restrictions in the combustion space, for it had been observed that the flame vibrations and acceleration which marked the setting up of a stationary wave during an explosion in the cylinder always began after the flame had travelled about three-quarters of its full distance. This "sensitive point" lies midway between the central loop and the end node of the vibrating column of gas.

The Influence of Restrictions at the "Sensitive Point" in the Combustion Space.—In the first experiments made in an attempt to influence the flame of an explosion at the "sensitive point" of the cylinder (15 × 6 inches), a diaphragm of wire gauze (10 mesh) was inserted at that point (about 11½ inches from the ignition end of the cylinder). Such a device might be expected both to chill the flame and to hinder the displacement of vibrating gases. It was remarkably effective. No mixture of pentane and air, initially at 15° C. and 2 atm., produced a pinking explosion, whereas under similar conditions but without the gauze, as already recorded, a stationary wave is set up on explosion of any mixture containing between 3·1 and 3·9 per cent. of pentane.

Figs. 1 and 2 are records of explosions of a 3·5 per cent. pentane-air mixture, initially at 15° and 2 atm. in the cylinder (1) without and (2) with the gauze diaphragm. There are no signs of vibrations in the latter, and the after-burning, following completion of the initial flame movement, is more diffused than in the pinking explosion (Fig. 1).

Such a device is no doubt impracticable in an engine cylinder, since it would cause pre-ignition. It should, however, be possible slightly to restrict the width of the combustion-space at the

" sensitive point " and this might be nearly as effective in hampering the displacement of the vibrating gases as the gauze diaphragm.

The diameter of the 15-inch closed cylinder at the " sensitive point " (*i.e.* 11½ inches from the ignition end) was reduced from 6 to 4 inches by the insertion of an annulus, 1 inch wide. Under these conditions, the sound of an explosion of a 3·5 per cent. pentane-air mixture, initially at 15° C. and 2 atm. was but little different from that of explosions of the same mixture in the cylinder without the restriction. The flame and pressure records, however, differed in several respects (*cf.* Figs. 1 and 3). With the restriction (Fig. 3) no vibrations could be observed either of the flame or of the pressure-record before the attainment of maximum pressure, but the development of pressure was gradual and the maximum was sustained during about 0·02 sec. A stationary wave was then set up and a " pink " of but moderate violence ensued. The records were, in general, similar to those obtained occasionally with benzene-air or cyclohexane-air mixtures at high initial temperatures and pressures.

No other position of the restriction was found to be effective. Thus, when the restriction was placed at another possible " sensitive point," about 3½ inches from the ignition end, the setting up of the stationary wave occurred as usual after the flame had travelled three-quarters of its distance from the ignition end. The effect of introducing two restrictions about quarter and three-quarter distance from the ignition end of the cylinder was not so great as that of one restriction at the three-quarter distance.

The effect of a similar restriction at the " sensitive point " in an engine cylinder would be equivalent to considerable retardation of the ignition. The piston would recede, causing a drop in the mean temperature and a change in the acoustic properties of the charge before a stationary wave could be established, so that no pink would occur. The amount of restriction should not, however, be so great as to affect materially the turbulence of the charge. These conclusions are being tested experimentally.

Department of Fuel Technology,
University of Sheffield.

DISCUSSION.

The President, in opening the discussion, thought the members would agree that they had listened to a description of experimental work of the very first importance, in connection with which he desired to ask a few questions. First of all it seemed that what was required to prevent pinking in the cylinder was something that

would catalyse the after-burning reactions. He wished to ask if the suggestion made in the last paper given by the authors had been followed up—namely, gas analysis of the products of combustion taken at various stages during the explosion. Was anything known chemically about the nature of the material behind the flame front? In some cases it seemed to burn quietly, but in other cases it was only made to burn by the impact of the shock wave reflected on to it. Furthermore, he suggested that some attempt should be made to correlate the work on spontaneous ignition temperature, to which reference had been made, and the nature of the propagation of the flame itself. As far as he remembered Weerman, of Holland, described (*J. Inst. Petr. Techn.*, 1927, **13**, 300—307) certain experiments on self-ignition temperatures, and he seemed to have obtained some correlation between the actual effect of anti-detonators in the cylinder and their effect on the spontaneous ignition temperature. He imagined that the engineers present would be more particularly interested in the authors' work on the effect of constrictions in the cylinder space, and he was perfectly certain they would like to ask questions on the very interesting point brought out that apparently pre-ignition was not the bugbear that most of them thought it was.

Prof. Brame said he agreed with the President that the work the authors had done had thrown a great deal of additional light on what actually was happening in the explosions described. One of the most important points which had been established appeared to be the effect of the reactions which took place behind the flame front. He was very glad that the authors had preceded the description in the present paper by giving a little enlightenment as to what was seen through the window, because he could discover nothing in the previous paper which threw any light as to whether the photographs were negatives or positives, but on the present occasion he noticed that a diagram of the window in the cylinder was given on each photograph so that the members were able to appreciate that the previous pictures were negatives. With regard to the chemical reactions taking place behind the flame front, it must be recognised that combustion in such cases was not a single phase reaction. There was a good deal more going on when a hydrocarbon like pentane burned to carbon dioxide and water finally than was expressed by the very simple equation which we were accustomed to write. The authors had referred to carbon disulphide and also to the action of steam. He did not know whether the experiment had been tried—he rather gathered that it had not—but it would be very interesting to know what the effect of steam would be with carbon disulphide in the cylinder. The steam was

playing a part presumably in the combustion of the hydrocarbon, but it was unlikely to play anything like a similar part in the carbon disulphide. He suggested it would be quite an interesting experiment. Personally he was rather doubtful about self-ignition temperatures and what they were going to teach. Some of the members might have seen recently a paper in the *Journal of Industrial and Engineering Chemistry* (1929, **21**, 134) on "The Determination of Auto-Ignition Temperatures." Anything more diverse than the results which could be obtained with auto-ignition temperatures according to the conditions under which the experiments were carried out it was impossible to conceive, and until some method was arrived at which gave auto-ignition temperatures which bore some relation to what happened in the cylinder of an engine, he did not think very great progress would be made in that respect.

Dr. W. A. Kirkby said there were many points he would like to discuss in the authors' very interesting paper. Firstly, in particular, in regard to the application of the subject dealt with to the internal-combustion engine, the question of "auto-ignition" was important. The effect of auto-ignition in its tendency to diminish pinking, or at least in not making pinking more pronounced, was interesting, and he desired to suggest that the reason for it was to be found in a study of flame movements in cylinders. During the course of an investigation carried out with Prof. R. V. Wheeler for the Safety in Mines Research Board, in which methane-air mixtures in a long cylinder were exploded and the ignition occurred simultaneously at two points in the cylinder, for example, at one end and very close to the opposite end, it was discovered that the pressure-time records and flame photographs did not show vibrations such as were obtained when single ignition took place at the end of a cylinder. Such conditions of ignition may be regarded as somewhat similar to the experiments described by the authors, in which ignition took place at one end of the cylinder, and auto-ignition occurred somewhere near the other end. Ellis and Wheeler had shown by their flame photographs that when two flames were independently started there was a hindering effect of one flame upon the other, so that there was a sort of delayed combustion taking place, which was perhaps not to be expected at first sight when double ignition took place. Whereas with single end ignition in the cylinder the flame movement had a vibratory phase, and the explosion was noisy, with simultaneous ignition at two points there was no vibratory phase and it was silent. He imagined that something like that was happening, although he would not like to be dogmatic about it. It seemed from some of his experiments that the resonance properties of the column of

flame gases was the important factor in determining the vibratory condition, and he presumed that in the authors' experiments that was the prelude to the shock wave which was at the moment considered to be essential for setting up pinking conditions. It would appear from his experiments that it was the column of flame gases in which the stationary wave system existed, and not the column of unburned and burned gases. He imagined that that was happening because there was a very great difference in density between the unburned column of gases and the column of flame gases. If auto-ignition occurred in the column of gases ahead of the flame front, more comparable densities were then obtained in the two columns of gases, and he said that perhaps that would destroy the resonance properties of the flame gas column, and consequently hinder the setting up of vibrations and the pinking effect. He desired to ask the authors to state what was the frequency of vibration of the flame front under the different conditions of cylinder experiment referred to that evening. He would also like to know if the frequency in the vibratory phase was constant, a matter of importance for the elucidation of the system of stationary waves. Was there any evidence from the experiments made that it was the column of flame gases which was the important factor in establishing and maintaining resonance? He presumed it was the case in all the experiments that the speed of the flame during the vibratory phase increased. Personally, he never could understand why that happened, and he wondered what the authors would say was the reason for it. It was an important point, because some definite connection seemed to exist between the vibratory phase and the increase in speed. In non-vibratory explosions the speed of the flame decreased as the end of the cylinder was approached, and he thought that to ascribe the increase in speed in the vibratory phase to turbulence was hardly an adequate explanation. One photograph had been shown indicating parallel alternate dark and light bands behind the flame front. He wondered if those bands would be found to be parallel if the camera were running at a higher speed and greater resolution was obtained. His own experiments seemed to reveal at first sight that the bands were parallel, but on resolution by a higher speed of drum camera they were found not to be parallel. Striations such as those described in the paper appeared in his own photographs of the vibratory phase, and although the absolute speed of the disturbance causing the dark bands had not yet been determined, he discovered that the speed of the disturbance was less at the beginning of the phase than at its end. The difference in speed was of the order that one would expect a sound wave to sustain in passing from a mean temperature such as exists at the beginning to that which

exists at the end of the period as deduced from the time-pressure records. It required a somewhat faster speed of drum camera to discover the whole story of the dark bands seen in the slides that evening. He desired to show a slide for the purpose of illustrating his remarks.

The slide showed a very enlarged portion of part of the flame movement. The flame was travelling from left to right, and the

film might be regarded as travelling vertically upwards. He thought the members would be able to see that there were incident and reflected waves at the end of the cylinder.

He wondered whether it was a fair question to ask if the authors would care to speculate about the origin of flame vibration. He supposed that the authors believed that their experiments indicated that the presence of the vibratory phase during an explosion in a

closed cylinder was a characteristic of pinking, although the maintenance of a shock wave was essential to produce that condition. It would also be interesting to know what the authors had in their minds when they suggested that it was the nature of the reactions proceeding behind the flame front which was the seat of the origin of pinking.

Mr. R. Stansfield said he had been wondering whether there might not be some difficulty in the application of restrictions to an engine cylinder. Considering the case of a cylinder with a turbulent head, the combustion space was already made much more compact than in the older type of head, and to place a restriction at, say, three-quarters of the width of the head from a plug positioned between the valves would probably so reduce the volumetric efficiency by wiredrawing the entering charge that more would be lost by the wiredrawing than would be gained by the restricting lip. Any addition of restrictions in the form of lips in cylinders must tend to damp out turbulence, and it seemed quite possible that the loss of turbulence might more than offset any gain due to the restriction. In their previous paper the authors referred to the behaviour of benzene and of pinking spirits, and it was suggested that the combustion was different in kind. During the discussion he (Mr. Stansfield) mentioned that benzene would not pink in a cylinder of $2\frac{7}{8}$ in. bore at a compression ratio of 10 to 1. Since then the same engine had been run quite smoothly on benzene with a compression ratio of 12 to 1 without pinking. The author had referred to pinking being obtained with benzene in the cylinder. Personally, he had had the same effect in an experimental cylinder head at a ratio of 11 to 1, and there the benzole pink was undoubtedly due to over-turbulence. A very slight reduction in the turbulence in the cylinder head made it run smoothly on benzole. He wondered if the authors could give any explanation of the behaviour of a bouncing pin fitted to the cylinder head. The pin operating a voltameter measuring the amount of bounce was sensitive to very small additions of benzole to a pinking spirit. In an engine with a head arranged to have a maximum compression ratio of 8 to 1 and moderate turbulence, very slight additions of benzole reduced the amount of gas collected. When the ratio was increased to 11 to 1 with over-turbulence, the addition of spirit to benzole had the opposite effect—*i.e.*, the rich benzole mixtures caused a large evolution of gas with pinking even with pure benzene, and blends with some of the pinking spirit caused less evolution of gas. As soon as the turbulence was decreased the pin behaved in a normal way. There was one other question he desired to ask. None of the flame photographs were complete. Did the glow in

the case of an explosion of benzene last for a longer or shorter period than the afterglow in the case of a pinking explosion?

Mr. E. S. L. Beale asked whether there was any possibility of the fact that carbon particles were obtained in the cylinder on explosion being due to local irregularities in the concentration of the hydrocarbons and the air, in the case of the standard mixtures due perhaps to insufficiency of time for thoroughly mixing. He desired to ask if in the authors' opinion the vibrations he obtained were considered to be just the prelude to the shock wave which travelled back through the partly burned mixture, whether they constituted the pinking themselves or whether the shock wave could be regarded more properly as constituting the pink. The pink, as he understood it, was the noise which was heard outside the cylinder, and it had a more or less marked constant frequency which might either be due to the cylinder head being struck by the shock wave or possibly due to the frequency of the oscillations obtained during the combustion.

Dr. G. B. Maxwell, in reply, said he proposed to comment first on a few of the points which had been raised late in the discussion. Mr. Beale had asked whether, in the opinion of the authors, the stationary wave or the subsequent shock-wave gave rise to the sound of a pinking explosion in an engine cylinder. He took it that the impact of the shock-wave on the cylinder head or walls was the origin of the sound since it was possible to set up a stationary wave in mixtures which would not pink at all readily in an engine.

With regard to Mr. Beale's question on the cause of the appearance of free carbon in certain explosions, he did not think that it was due to bad mixing. The smoke in the residue in the closed cylinders was only found after a pinking explosion—this could be compared with the smoky exhaust of a pinking engine—and was apparently unchanged in amount whether the mixtures were prepared in the explosion cylinder or first made up in holders, stirred and allowed to stand before use.

Dr. Kirkby had misunderstood the authors if he thought that they considered "auto-ignition" reduced the violence of the pinking explosions in their experiments. It had little or no effect. The auto-ignitions occurred so late in the explosions that perhaps the hampering effect of the second flame on the first had no time to become appreciable. In an engine cylinder matters would be still more complicated by the turbulence of the charge. The spacing of the striations in the photographs showed that the period of the stationary wave was approximately proportional to the cylinder length and inversely proportional to the initial pressure/density

ratio of the charge. With a 15 in. cylinder, 6 in. internal diameter, using pentane mixtures initially at 17° C. and any pressure, the period was about 1/1200 sec. The authors had considered the striations to be due to the alternate glowing and darkening of partly burned gas at and near the nodes where the particles were alternately compressed and rarefied. As far as could be judged the glow at one end of the cylinder coincided in time with a dark patch at the other, which would be the case with nodes at each end and a single loop in the centre. Dr. Kirkby's slide threw fresh light on the question of the cause of the striations and the subject would have to be more fully investigated. That the origin of the disturbances lay in the hot gases through which flame had once passed seemed clear from Dr. Payman's photographs, but he would not like to speculate on the nature of the disturbances.

The President had asked a question with regard to the investigation of the chemical nature of the partly burnt material behind the flame front. Dr. Ellis was carrying out work on these lines at Sheffield under Professor Wheeler. The other point to which the President and also Professor Brame referred related to the effect of dopes on self-igniting temperatures. In his opinion the self-igniting temperatures of fuel-air mixtures had little bearing on the tendency of such mixtures to pink. It was rather the effect of dopes on the reactions proceeding once ignition had been effected that should be investigated. Professor Brame had also asked if the effect of steam on the combustion of carbon disulphide had been examined. The authors had not tried steam with carbon disulphide, but they had examined the effect of steam on the combustion of carbon monoxide. Up to a certain optimum amount steam accelerated the combustion of carbon monoxide, a non-pinking fuel, but had no other effect. The effect on CS_2 was known to be similar, from the work of Prof. H. B. Dixon.

Mr. Stansfield had raised a very important practical objection to the use of restrictions in the combustion space of an engine. The authors had realised the possibility of loss of volumetric efficiency and of turbulence by the use of such restrictions, and considered that further work should be done on these lines. With regard to the pinking of benzene blends in sensitive, over-turbulent heads, it was possible that the greater rate of flame propagation and pressure development of benzene (as compared with the paraffinoid constituents of motor spirit) was the cause of the apparent pinking.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

A meeting of the Rumanian Branch of the Institution of Petroleum Technologists was held at the Industrial Internationale Club, Ploesti, on March 1, 1929, the chair being taken by Captain J. E. Treacy. The following paper was read :—

Re-Pressuring of Oil Sands.

By Gwyn Elias, B.Sc. (Associate Member).

Of all the problems confronting the production engineer to-day, there is none of greater moment than that of increasing the yield of oil from a sand—*i.e.*, the ultimate, and not the daily, yield.

Most estimates indicate that 70 to 80 per cent. of the oil contained in a sand is not recovered by the usual methods of production. It is very probable, however, that this estimate of non-recovered oil is too high for cases where there is an edge-water of high hydrostatic level. An edge-water of this nature must provide a fairly effective drive, except in cases where wells are widely spaced along the strike line and where wells are produced at a high rate ; it can then be expected that there will be a tendency for the edge-water to advance in tongues instead of at a steady speed along its whole face, and large pools of what should be potential production would then be entrapped by the water. This is a suggestion which is put forward to account for the peculiar behaviour of some of the wells producing at one time from the third sand in Stavropoleos-Moreni.

Of the various solutions (or partial solutions, as no method of recovering 100 per cent. of the oil in a sand has been devised) to this problem of increasing the recovery from a sand, the ones offering the greatest economic possibilities are those which involve the injection of water, air or gas into the producing sand with the intention of driving the oil to the areas of low pressure—that is to say to the producing wells.

In this paper it is not intended to discuss the first method, water-drive, which would seem, up to the present, to have only limited application, and to have only attained real success in the

Bradford field of Pennsylvania. On the other hand, the injection of air and gas has resulted in very many successes in different fields, and it is this aspect of oil-driving which it is intended to discuss now.

The original idea of gas-drive was to inject gas, or air, into a commercially exhausted sand at selected points, with the intention of pushing as much as possible of the oil remaining in the sand to the producing wells. This method of operating has been still further developed until now gas is actually being put into the sand in the early life of the field, during the stage of flush production, so that, besides actually driving the oil, the rock pressure will be kept as nearly as possible to initial.

If the conditions existing in an oil sand at the moment when it is tapped by the discovery well are known, then, by a properly organised drilling programme and the application of the present knowledge of the production engineer, a greatly increased recovery of oil could be obtained over that usually found. The most important information needed is the initial rock-pressure at different points in the pool as they become tapped by wells, and the natural gas-oil ratio (the amount of free and dissolved gas in each barrel of oil as its exists in the sand). It is this gas, compressed in the oil in its natural condition, which is our great ally, although only too frequently this is not fully appreciated. Fortunately, the day has passed when gas was blown unnecessarily into the air and wasted. It is now considered by some to be an almost equal crime to produce gas from the sand at any above the necessary minimum rate. This point of view is not unreasonable when it is remembered that before the gas is produced it does three things: firstly, it reduces the viscosity of the oil in proportion to the amount of gas dissolved in the oil, which in turn depends on the rock pressure; secondly, it travels from areas of high pressure to areas of low pressure, the wells, bringing the oil with it to the bottom of the wells in spite of the high resistance offered to it by the sand; and thirdly, it lifts the oil towards the top of the well. Therefore, to prolong the time during which the gas will give these benefits is to prolong the life of the field and increase the ultimate production. To get the maximum from the potential gas energy of the pool, properly controlled back-pressures should be applied, gas-drive operations should be started early in the life of the field and the gas-oil ratio kept down by applying gas-lift in the early life of the individual wells. Many experiments have been carried out and figures are available showing the effect on viscosity due to the amount of gas dissolved in a crude. The figures vary somewhat for different types of crude and different natural gases, but the effect can be stated by saying that an average crude with a maximum amount of gas in solution

at a pressure of 500 lbs. sq. in. will have a viscosity about equal to that of kerosine, and also reduced surface tension. The effect of this on a crude which has to pass through the pore spaces of a sand can well be realised.

It is when the question is looked at in this light that the contention of many production engineers that the gas is more useful in the sand than as a marketable product is appreciated, but this will be dealt with later.

If the *natural* gas-oil ratio of a pool is established before wells are producing from it, can the oil and the gas then be produced in the same proportions? This very desirable method of operating is probably never attained in a normal field. Dominguez field provided an excellent example of what can be done by properly controlling producing wells. Experiments indicated that the original gas content of the sand was 344 cu. ft. per lb., but under flowing conditions 2400 cu. ft. were produced with each barrel; in other words, with each barrel of oil produced the oil remaining in the sand was robbed of 2056 cu. ft., the equivalent of the gas content of 6 bbl. of oil which might be considered as dead, or left without energy. By using gas-lift and properly regulated back-pressures the gas-oil ratio was reduced to 1037 cu. ft. bbl., which meant that the equivalent of the gas content of 2 bbl. of oil was being taken in excess out of the sand.

If a flush field is produced inefficiently and re-pressuring is left until the field is almost commercially exhausted the ultimate yield of the pool must be very considerably less than when properly controlled back-pressures have been used from the beginning and re-pressuring operations commenced in the early life of the field. In other words it is better to keep the field young than to rejuvenate it.

To assist the operator in obtaining data of conditions at the bottom of the hole, data which greatly helps when planning drive operations, a thieving device has been developed by Sclater and Stephenson which brings from the bottom a sample of the oil, which can then be examined in its bottom-hole condition, together with a record of its temperature and pressure. This will greatly assist in displacing assumptions by accurate knowledge.

Air and Gas Drive in Partially Depleted Sands.—Before attempting either drive or pressure maintenance operations, it is of importance to obtain as much data as possible on the conditions existing in the sand. Of first importance is the rock pressure at different points in the sand, and next the gas-oil ratio of the producing wells. The former can be found with a fair degree of accuracy by shutting in the casing-head and taking the shut-in pressure

and hydrostatic level of the liquid in the hole. As some wells build up slowly, the final pressure reading must be taken when the gauge no longer shows a rising pressure. The gas-oil ratio is found in the usual way from the oil and gas production reports or from special tests made at individual wells in cases where gas production reports are not kept.

The key wells, through which the gas or air is to be injected into the sand, are selected according to local conditions, keeping the following considerations in mind:—

The key wells should benefit the operator carrying out the drive without benefiting the neighbours, unless the work is being done in co-operation with the latter.

The key wells should, to begin with, be each within a group of wells which it is intended should benefit from that key well. As an experiment one pressure well might be chosen for each group of four to six producers.

The position of the key wells on the structure is not of great importance, as sand conditions usually have the deciding influence on the direction of the drive. Experience so far does not show that the injected gas will take any definite direction in relation to the structure. However, key wells situated somewhat higher up the structure than edge-water will help to keep the water back.

Where wells are known to be in a tight sand, they should, if satisfactorily placed otherwise, be chosen as pressure wells. The only method which the author can suggest for determining which wells are located in tight sand is by the slowness with which they build up their rock pressure when taken off production. Perhaps this method is not conclusive.

Having selected the pressure wells they must be put into condition for gas injection, unless it is known that the casing is in sound condition. If not, the gas might be lost in a thief formation or be returned to the surface behind the defective string of pipe. To prevent loss through possibly defective casing it is usual to run a string of tubing, with a packer on the bottom, to the top of the perforations. Sometimes a simple rag packer is used and two or three sacks of cement poured on top. A better practice, which will allow the pressure well to be put back on production, is to run two or three joints of 4 in. on the bottom of the tubing, with a back-off joint above the 4 in., and cement the 4 in. at the back. Naturally the hole must be clean to the bottom of the perforations, and if the sand is very tight, and refuses gas, shooting will generally effect a cure. Abandoned and suspended wells must be well plugged right at the sand.

The injection pressure should not considerably exceed the rock pressure at the key well; if the input gas is forced too quickly

into the sand it might break through into loose places and by-pass the areas of highest oil content.

By-passing or channelling is the most troublesome condition met with in re-pressuring, the gas being only too liable to avoid regions of tight sand which will probably be the places of high oil content, and therefore the very places where it is intended the drive should have effect. If the conditions at the producing wells indicate that the gas is channelling towards one of them, preventive steps must be taken by holding a back-pressure on that well or, in extreme cases, of shutting in that well entirely. In some cases the channelling becomes so persistent that it is necessary to change one or more of the key wells; for this reason it was mentioned above that in conditioning key wells it must be considered that they might later have to be put back on production.

Driving does not usually yield quick results, three to six months being quite a usual period to wait, although the author knows of one well which showed a marked production increase within 36 hours of the time that gas was put into the neighbouring key well.

A sudden increase in input gas or decrease in pressure at a key well is a warning to watch the producing wells carefully, as probably the gas is blowing through to one of them.

If an insufficient quantity of gas is being put into the sand, it is better to increase the number of input wells rather than increase the pressure at the existing wells.

To be able to carry out drive operations intelligently, accurate records must be kept of the behaviour of the input and the producing wells; it is then possible to plot, periodically, on a map, the direction and intensity of a drive. Such records also enable the operator to follow up the economic effects of the operations.

Compressors should be mounted in a central installation rather than as individual units at pressure wells. This would allow for future rearrangements of pressure wells without having to move the units, and more flexibility in the distribution of the gas and usually better supervision of the machinery is possible. Where pressure wells are fed from a main header, suitable arrangements must be made to prevent any one well "hogging" the gas, to the loss of the others.

The above remarks apply equally to the use of air or gas in drive operations in commercially exhausted, or almost commercially exhausted, fields. But for drives in this type of field the author is in favour of the use of air rather than gas, being influenced by the following factors:—

Gas will not usually be available except in the neighbourhood of flush fields.

Considerable quantities of gas might be lost in an experiment which proves unsuccessful.

Experimental work shows that gas is more readily soluble in oil than air ; the dissolved gas will reduce the viscosity of the oil, but only to a small extent in low-pressure formations. The part of the gas absorbed by the oil is not effective in driving it, so that air will have more of a driving, or piston, effect. This characteristic of air seems to be proved by operations in some fields, although no very definite conclusion has yet been arrived at.

Air has some disadvantage, as after some time it will so dilute the gas produced as to make it useless for fuel purposes, and to return the mixture down the input wells is dangerous owing to the possible formation of explosive mixtures of air and gas. Air does not appear to oxidise the oil but, where water is present with the oil, serious corrosion problems may occur.

That gas drive does frequently reduce bottom-water and edge-water was amply proved in the Turbeville field and others.

As to the ultimate yield of a successfully re-pressured field, no final data is available, but by comparison of the decline curves of production from re-pressured sands with the normal decline curves there can be little doubt that the operations are commercially satisfactory in many fields. In many cases the operations justify themselves in a very short time, and even before the production curve falls to the level existing before re-pressuring work was started.

Pressure Maintenance Operations.—The logical development of gas drive operations in partially depleted sands is to apply the same principles during the early life of a field. Besides driving the oil the injection of gas has as an object the maintenance of the rock pressure. Results so far obtained amply justify the confidence shown by early supporters of such a scheme.

In pressure maintenance operations key wells are drilled, or chosen from existing producers, before an appreciable decline in rock pressure takes place. Gas is put into the sand at high pressures, as much as 1500 lb. having been used. Gas is more readily obtainable in a flush field, and should be used instead of air, and as the rock pressure is not much short of initial, it allows the operator to take full advantage of the correspondingly high solubility of gas in the oil, with the consequent reduction in viscosity. Some production engineers advocate the use of wet gas for re-pressuring, this being more soluble in oil than stripped gas.

The only pressure maintenance which the author has seen operating, apart from the type of gas drive described above, was giving very satisfactory results. There were four corner locations, 610 ft.

spacing, gas-lifting 1800 bbl. daily. The centre location was drilled, and came in as a natural flowing well with 700 bbl., bringing the total production for the property up to 2500 bbl. The flow in this fifth well was killed, and 3,000,000 cu. ft. of gas put into the sand daily at a pressure of 600 lb. In a short time the four original corner producers showed a marked increase and went on to natural flow, reaching a total of 2800 bbl. at the time the author was last in the field, an increase of 1000 bbl. over their original production and an increase of 300 bbl. over the production of the property when producing from five wells.

In describing the re-pressuring work done by the Marland Company at Seal Beach, A. H. Bell mentions their first pressure well, making 250 bbl. of oil and cutting 60 per cent. emulsion. There was a high fluid level and the initial pressure of the input gas was 1500 lbs., falling later to 1420 lbs., taking 1,500,000 cu. ft. per day. A 50 per cent. increase in production was shown by some of the up-structure wells, with small production increase and marked water decrease in some of the down-structure wells. Later, other pressure wells were chosen and from carefully kept observations it was seen that there was a general tendency for gas to migrate up the structure and to hold back edge-water. This indicates that pressure wells located slightly up the structure from encroaching water might, in general, give better results than in the case of the "five-spot locations."

Many operating companies would probably be reluctant to return marketable gas to the producing sands, but a Californian engineer has shown that each 4000 feet of gas injected in one Californian field recovered an additional barrel of oil and 6 gallons of gasoline, valued at $1.48. The cost of compressing the input gas was 5 cents per 1000 cu. ft., leaving a net profit of $1.28, or 32 cents per 1000 cu. ft. of gas which would have been sold to a gas company for 6 to 10 cents per thousand. In Seal Beach each 490 cu. ft. of input gas produced an additional barrel of oil.

Gas Storage.—Producing sands are now being used for the storage of gas during periods of flush production. This operation differs from pressure maintenance, and instead of trying to move the oil towards the producing wells, by creating pressure differentials in the sand, gas is injected with the intention that it should remain there, so that the producing wells have to be handled in such a way as to reduce to a minimum the underground circulation of gas. This is done by holding sufficient back pressure at the wells and by shutting-in entirely those wells which produce enough gas to neutralise the efforts towards gas storage. Inlet wells should be located high up the structure where the higher gas content of the

sand allows, because of the compressibility of the gas, the reception of larger quantities.

In Dominguez field the two major operating companies have been co-operating for 7 months in the storage of gas. Each company arranged to inject 10,000,000 cu. ft. of gas per day, part of this quantity coming from Long Beach, the gas being put in through 11 inlet wells. Of the 32 wells producing after the inlet wells were taken off production, 15, which had been producing by gas-lift, returned to natural flow and some of the others, which were previously flowing openly, became producers under back-pressure.

In spite of 11 wells being taken off production and high back-pressures applied at the others which were flowing, gas-lifting or pumping, yet the production decline curve for the field is only following a fairly normal decline. It is estimated that about 80 per cent. of the input gas is being retained in storage in the sand.

The above illustrations are given to show once again the advantages of co-operation between the companies operating a field. That co-operation can be attained in spirit as well as in written agreements between companies as is shown by the action of one company in Dominguez putting unnecessarily high back-pressures on two boundary wells because the other company's two offsets had, for technical reasons, to be produced with equally high back-pressures.

DISCUSSION.

Captain J. E. Treacy said the subject of the paper is interesting for the production men. There has not been much of this work attempted in Rumania up to the present time, and if those taking part in the discussion would refer especially to Rumanian oilfield conditions it would be of interest to every one.

Mr. C. A. Bauduin said he would like to say that about two years ago there was a trial for several months of the Marietta process in the Moreni Fields for the Drader sand. As a whole it could not be called successful.

The reasons for disappointment were that the key-well was not in the condition it should have been and that the area in which gas was driven was, for the larger part, still producing by the bailing method. Therefore, despite measuring of intake gas and measuring the outflow of gas at individual wells with as much accuracy as possible, the application remained far from perfect to obtain conclusive final results.

The wells showed undoubtedly the influence of the gas drive. The gas used was dry gas.

The author stated that he preferred air rather than gas. Air has disadvantages; it makes the oil more viscous than gas. If the pressure is low, it is better to have the oil as fluid as possible and therefore the use of gas instead of air is preferable. The use of waste propane from a gas plant with stabiliser is better still.

The practical results of gas drive can only be determined after a very long time, and even when one has obtained an increased field production it remains still questionable whether the ultimate recovery will be increased, too. The most important condition of success will be the ability to control the outflow of gas with proper means of shutting in. Unfortunately, the co-operation between companies is not as yet so advanced that simultaneous application of gas-drive under similar conditions can be tried out here, as is the case in some instances in America.

Mr. Ian Rutherford said that the last speaker had mentioned the use of air instead of gas. He had pumped air into the oil horizon by a compressor and, on producing the well subsequently by bailing, found the quality of oil considerably affected, especially the setting point, which was raised from 10° C. to 28° C. On continuing bailing the quality improved, but on each subsequent use of air the same effects were noticed. He would expect the same lowering of quality to be noticed in any well effected by pumping air into the oil horizon.

Mr. J. M. Leitch said an example of an involuntary drive by air might be quoted from the Tontesti field. There are three wells about 40 meters apart, forming a triangle, one of which was placed on air-lift and the production increased slightly. The production of the other two wells increased considerably, one of them by 75 per cent. When the first well was taken off the air-lift the production of the other two wells fell below the amount obtained prior to air-lift operations, and no amount of bailing could bring them back to the original figure. The first well was again placed on air-lift and the production from the remaining two was again increased.

Mr. E. T. Hancock said he understood from the best authorities that only from 15 to 25 per cent. of the oil which is originally in the formation is recovered. The question naturally arises as to what must be done to overcome the forces which are holding the remaining portion of the oil in the pores of the sand? In Rumania the air and gas drive has not been used to a sufficient extent to give many results; but it seems that one of the principal difficulties, when it

is put into practice, will be channelling. That will apply more to the Meotic than to the Dacic. Perhaps the Dacic sands are more uniform in character, particularly in reference to the Moreni and Drader horizons, and would respond better to the air and gas drive than the sands in the Meotic. From experience with the Meotic there must be channels which are probably determined mainly by the coarseness of the material, the size of the sand grains themselves probably being the principal factor. From a study of the cores we find a good deal of the sands exceedingly fine, both particles and pores being very small. It is known that in pores of a certain character there are certain forces which are active principally in capillary pores. Owing to the fact that it has been found that one well is influencing another at a considerable distance, it will be found that one of the things which will upset the air and gas drive will be the tendency of the air and gas to shoot off along definite lines and by-pass certain areas. Not necessarily small porosity, but where openings are very small a large quantity of oil is by-passed by the air or gas. It, therefore, seems that once this process is put into practice, one of the essential things will be for the companies to get together and try and carry it out in a scientific way. For instance, one of the best situations for using the air and gas drive where the company has a large tract of territory and wells regularly arranged would be to force the air and gas down a row of wells along one side of the field and follow the effect of the air and gas in the direction influenced.

He desired to raise a point as to the length of time needed to get results. Regarding the influence of wells on one another he cited an instance of three wells practically in a line. When the middle well came in it did not affect the first well, but when the third well was brought in it immediately influenced the first well, showing that the influence passed the middle well and was carried to the third. He would expect results almost at once in some wells, at least.

Mr. Gwyn Elias, in reply, said he wished to thank Mr. Bauduin for giving the interesting information about the only really serious attempt of air and gas drive in Rumania. He presumed that the producing wells were old wells which had yielded a considerable amount of sand, thus having the best conditions for channelling.

Regarding the use of gas for even low-pressure fields, gas is more soluble in the oil, reduces viscosity and eases the drive effect, while air is more soluble in oil up to a critical pressure. The dissolved air in the oil reduces the viscosity in the same way as the gas. These results have been obtained by one series of experiments and not generally confirmed. They have shown that up to the critical pressure, about 220 lbs./sq.in., air is more soluble than

gas in oil and will, in the same proportion, reduce the viscosity of the oil. He thought the injection pressure was less than 200 lbs. in the case mentioned. In that case, air would be more soluble than gas and might have given better results.

He agreed with Mr. Bauduin that old wells are not worth attempting for drive operations owing to the production methods then used.

In reference to the use of air in place of gas, air does spoil the quality of the oil by affecting its gravity, and if a weak mixture of air and gas comes with the oil it is not suitable for fuel purposes and the gas is usually lost.

He had never heard of a condition like that stated to exist in the Tontesti wells. In some fields it had been demonstrated that wells put on gas lift had a drive effect to neighbouring wells. There is too much back pressure on the sand and probably by using big tubing and greater quantities of gas, the back pressure on the sand would be decreased and the drive effect would be lost. In Bana, one company was using gas lift on a well which seemed to have a drive effect on a neighbouring company's well.

He was not sure whether Mr. Elder advocated the use of gas drive to one sand and then drilling on to lower sands, but was of the opinion that that was the way to operate. The most rational way is to exhaust as completely as possible each sand and then go deeper. Water drive seems to be successful in the Bradford field, the peculiar sand structure seems to respond to the injection of water. In other fields, the water channels and traps pools of oil that will never be recovered, unless a well is drilled in that exact spot, and that would probably never be attempted.

He agreed that channelling would probably be the great difficulty in Rumania, and that the Dacic sands would probably never be suitable for gas driving in old fields. There is so much difficulty in by-passing and channelling in the most exhausted parts of the sand.

Regarding Meotic sands, Mr. Hancock refers to the textures obtaining there as not being good conditions for gas drive. The first sand seems to be complex of sands and shales, and presumably some of those sands, which are separated from each other by bands of shale, will vary in pressure and would result in the sands of lower pressure hogging all the gas and leaving the sand or sands which contain the most oil unaffected by the injected gas.

In the special case mentioned by Mr. Hancock, there is proof of the variable zone of influence of one well on another, distant wells sometimes affecting one another without influencing intermediate wells. This must be due to streaks of tight sand which protect certain areas from influence and, no doubt, accounts for the unexpected directions often taken by injected gas in drive operations.

There seems to be a considerable amount of interest in the difficulties which would be encountered if an attempt is made to carry out drive operations in Rumania, and some of the causes why drive operations might not be successful, at present, are :—

1. The fields are owned by numerous operators and make co-operation difficult. Where an operator owns very small tracts the gas drive is not satisfactory, as it is impossible to gauge the direction of the gas drive and probably a neighbour would get the benefit.

2. There are certain sands which probably are suitable for gas drive—*e.g.* (*a*) In the Dacic sands at Bana, the sand is lenticular; (*b*) the third Meotic sand in Gura Ocnitza and Moreni is not suitable for the drive, owing to being flooded by edge-water, in itself an effective drive; (*c*) the first Meotic sand is probably not suitable, as mentioned in the reply to Mr. Hancock; (*d*) wells have been spaced very close together and produced in such a way as to bring up great quantities of sand which would result in channelling and by-passing, and this difficulty it is impossible to overcome; (*e*) the overlying beds of shale have caved in and probably shut off areas of sand. He had in mind some wells, previously good producers, which had gone off oil and produced clay which had caved in from above the sand. It is clear, however, that more modern production methods should give fields which will be suitable for gas drive operations.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Trinidad Branch.

THE TENTH ORDINARY MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held in the Club House of the Trinidad Leaseholds, Ltd., at Forest Reserve, Fyzabad, on Wednesday, February 27, 1929, Mr. A. Frank Dabell, M.I.Mech.E. (Chairman), presiding.

The following papers were read :—

Some Notes on Cretaceous Occurrences at Lizard Springs, Trinidad.

By P. W. JARVIS.

This paper sets out the fossil evidence upon which certain core and pit samples are ascribed to the Cretaceous.

Of about two hundred and fifty samples collected by Mr. Skelton at Lizard Springs, foraminiferal examination showed that a large number contained Cretaceous fossils. As a check, similar samples were washed out in Mr. Skelton's office by Mr. A. Mathews and gave almost identical results.

The Cretaceous fossils obtained from the Lizard Springs are almost identical with the fossils from the "Hobson's Clay" or "Spiroplecta Clay," a bed directly overlying the "Argiline" of San Fernando Hill, and underlying the Mount Moriah Beds.

In the Cyclammina Clay and the Marls the fossils are visible to the naked eye. In these Cretaceous beds they are invisible even under a hand lens. It is necessary to remove the large quantity of fine clay from the sample, and the fossils can then be seen in the residue under the lens.

If the slides of fossils extracted from the Lizard Springs samples may be examined they will be seen to contain assemblages of from ten to twenty or more species. In most of these assemblages are found specimens of three small fossils, *Rzehakina epigona*, *Spiroplectoides clotho* and *Nodosinella valascoensis*, and in some of the specimens they are present in large numbers. Further close examination of these slides shows that these assemblages are substantially the same, and that the specimens of species on one slide are almost identical with those on the others.

Rzehakina epigona.—This is one of the finest markers of the Upper Cretaceous beds in Trinidad. It is found in them in large numbers, and up to the present has not been found in any other bed. This fossil is very distinct. There is no difficulty in distinguishing it at once by its shape, the construction of its shell, the arrangement of the chambers, and also the peculiar depression in the centre of the shell. It was first recorded from the lowest Eocene beds of Austria, since when it has been found in the Velasco Shales of Mexico, considered by geologists there to be of Upper Cretaceous age. Being only about one-twentieth of an inch in diameter, its small size may seem to make it unfavourable for use as a zone fossil. But the defect can be remedied by magnifying it one hundred times when it appears to be five inches in diameter.

Spiroplectoides clotho.—This is another excellent zone marker, being found only in the Upper Cretaceous beds. It was first recorded from the Cretaceous shales of Galicia, but has also been found in the Velasco shales of Mexico, and in their equivalent bed in Texas, the Navarro shales.

This fossil was previously known as *Spiroplecta annectens*, and from the abundance of specimens found in the clay in Mr. L. M. Hobson's garden on the Pointe-a-Pierre Road, San Fernando, this exposure was named the Spiroplecta Bed.

The megalospheric and microspheric forms of this creature are very different and might easily be mistaken for different species.

Nodosinella velascoensis.—This is another good marker, but inferior to the previous two as it has descendants in the Eocene beds here which are somewhat like it though not identical. This species might easily be taken for a Nodosaria, but on close examination its shell will be seen to be constructed of extremely fine sand grains cemented together with a transparent cement, while Nodosarias have calcareous shells.

In addition to these three are many other species at Lizard Springs that are also found in the Velasco shales. There is at least a 50 per cent. agreement between the two faunas, and it is on this account and not on the occurrence of one or two species only that the beds are taken as Cretaceous.

It is wonderful how the fossils from Lizard Springs correlate with these of the Velasco Shales. Over one-half of the species found in Trinidad are found fifteen hundred miles away in Mexico, and the individuals are almost identical. When they are further studied this high percentage will no doubt be increased.

To assist those who wish to study these interesting fossils, as complete a set as possible will be deposited in the museum of the Royal Victoria Institute in Port-of-Spain.

The importance of studying foraminifera as guides to the strata has, in the past, been overlooked by most geologists visiting Trinidad ; but these small fossils are now receiving considerable attention by all the oil companies here. In the United States a few years ago there were only three micro-palæontologists employed by the oil companies : now there are over three hundred.

Mr. Skelton declares that the Cretaceous beds of Lizard Springs are oil-bearing, and that a well penetrating them to a depth of about 600 ft. has yielded a fair quantity of high-grade oil.

Is it possible that these beds are the " mother rock " in which the oil originated ?

Is it possible to find out whether the oil has migrated into them and from which bed ?

Are there other beds of Cretaceous age in Trinidad that are oil bearing ?

Are the Cretaceous beds in Venezuela, Mexico and Texas oil-bearing ?

Is there any evidence to show that the oil found at Tabaquite, Palmiste, Fyzabad and Vessigny is not probably from the same source ?

Is there any evidence to show that there is any oil in Trinidad of Miocene origin ?

In illustration of his paper the author exhibited :—

1. Samples of the material claimed to be Cretaceous.

2. Samples of the fossil bearing residues after disintegration and removal of the clay by washing and sieving.

3. Slides of mounted fossils from the Lizard Spring samples.

4. Slides of fossils from the Hobson's Clay.

5. Enlarged figures of *Rzehakina epigona*, *Spiroplectoides clotho* and *Nodosinella velascoensis*.

The Chairman announced that Mr. Jarvis asked that discussion of his paper be deferred until the next had been read.

Some Notes on a Portion of the Lizard Springs Anticline.

By R. H. Skelton.

The area under review consists of a rectilinear four-sided block whose S.E. corner has co-ordinates approximately latitude 10° 11′ 45″ North and longitude 61° 4′ 21″ West, or in other words two miles east of the southern terminus of the Government section of the Rio Claro Guayaguayare Road.

Up to date five wells have been drilled on the plot, four of them in a line across the strike of the measures, and the fifth offset 300 ft. to the West. Three were drilled by a small Calyx Rotary outfit, and two by a No. 28 Star Rig using cable tools.

The tract is extremely hilly, especially where covered by rocks of the Moruga formation. Where the softer pre-Morugas occur the relief is more gently undulating. It is entirely covered by "highwoods" consisting largely of the mora tree; there is also a good deal of secondary vegetation whose upgrowth is due, no doubt, to past forest fires. Penetration is usually only effected by extensive cutlassing.

While the Moruga formation is well exposed in stream-beds, it is rare to find outcrops of the softer pre-Moruga rocks. The writer came across such exposures in only one instance. In the areal survey, therefore, reliance had to be placed almost entirely on pitting.

In the surface examination of the area 160 pits were sunk and 855 ft. of trenching done. These afforded 235 samples, all of which were washed out and examined for lithological characteristics and foraminiferal contents. Time did not allow exact examination for heavy mineral residues to be carried out, and, apart from the extraction of all forams, rough comparison only of the residues from washings could be made.

The forams extracted from all samples were picked and mounted for record by Mr. A. Mathews of the T.C.O. Duplicate samples were in 50 per cent. of the cases sent to Mr. Jarvis for similar treatment, and this proved of great value in providing a control on our office identifications of the fauna.

With regard to well samples, 136 core and bit samples, representing a footage drilled of 3690 ft., have been washed and the forams picked and mounted. This averages one sample to every 37 ft. of well drilled, or on the assumption of an average dip of 60°, one sample to every 18½ ft. of ground measured stratigraphically. As entire reliance cannot be placed on bit and bailer samples from

a well drilled by cable tools, a coring device capable of taking cores 1 ft. in length was used in the Star wells, and this proved very successful. Where bit samples taken from the same point were found to be at variance with those taken with the core barrel, the former were disregarded.

Something over 1300 forams from surface samples and wells were mounted and over sixty different forms identified. At the same time lithological characteristics were by no means disregarded and, although lateral variation is extreme in this district, it was usually found that similar appearing rocks had approximately similar faunal content.

It may be remarked here, for the benefit of those who are contemplating an examination in the Lizard Spring district, that pitting is by no means expensive, as the alluvium is shallow and it is rarely that a pit has to be carried more than 5 ft. deep.

All identifications done in the writer's office were based on the experience of Mr. Jarvis and on Prof. Joseph A. Cushman's book, "Foraminifera : Their Classification and Economic Use."

Stratigraphy.

Great difficulty has been encountered in working out the stratigraphy of this area owing to the highly folded and faulted nature of the structures. No deposits of Eocene or Oligocene age are recognised at the surface, and, as Cretaceous rocks are found outcropping, it may be that the terrain was above water during Eocene and Oligocene times, becoming later submerged to receive Miocene deposits. On the other hand, the presence of Cretaceous sediments may be due to thrust-faulting alone, although, as will be shown later, this does not seem to be likely.

The deposits noted at Lizard Springs are of the Tertiary and Cretaceous age, and may be classified, in descending order, as follows :—

Tertiary	– –	Lower Moruga Formation. Lower Naparima Formation. St. Croix Formation.
Cretaceous	–	Cretaceous silts and clay.

The sands and sandy clays and sandstones of the Lower Moruga formation are too well known to need further description ; it suffices to say that in Lizard Springs they present identical facies with the Lower Moruga of the oilfields of South and South-west Trinidad.

The Naparima Formation is represented only in its lower part by the Green-Clay and foraminiferal marls and sands, presumably equivalent in age to the green clay and upper marl of Princes Town and the Naparima district generally. In Lizard Springs it would appear that the intercalated marls and sands are above the Green

Clay, whereas in the Naparima district they are known to be below it. This may possibly be a local illusion due to extensive overthrusting, or these two members may conform to the condition noticed by Waring in page 59 of his paper, "Geology of Trinidad," where he says: "In some places the Green Clay and the Princes Town Marl deposits would seem to be better considered as members, or facies, of one thick formation of foraminiferal clay."

Be that as it may, the total thickness of the Naparima marls and clays at Lizard Springs seems to be only some 500 to 600 ft., and no harm will be done if they are treated as a single group presenting a marly-sandy or green clay facies as the case may be. It seems quite certain that at Lizard Springs the Forest or Cyclammina clay and the Forest sand series of the oilfields of S.W. Trinidad are absent or, if they have an equivalent here, it is unproductive. The only sandy beds found in the pre-Moruga area are associated with the marls and the supposed St. Croix formation just south of the line of seepages.

The criteria for placing the above-described beds in the Naparima formation are :—

(*a*) Lithological similarity with the typical Green Clays of the Naparima belt.

(*b*) The almost universal presence of gypsum.

(*c*) A fauna consisting of :

Ammodiscus incertus.
Cyclammina cancellata.
Nodosaria.
Textularia.
Trochammina.
Truncatulina Uvigerina.
Haplostiche.
Rhabdammina.
Globigerina.
Reophax.

Cyclammina and *ammodiscus* being predominant.

(*d*) The predominance of globigerina in the marly portions.

(*e*) Their position in relation to the known Moruga beds.

Immediately south of the Green Clay-marl formation just described occurs a belt of supposed Cretaceous sediments which will shortly be described. Immediately south of this Cretaceous belt a bed ranging from 100 to 200 ft. in thickness appears whose lithology fits in with that of the upper St. Croix in other parts of the island. These criteria consist of small quartzite pebbles and grains of black chert, which occur in a narrow sandy member towards the base of the bed. In the main the bed is formed of blue-black and brown-black oil-smelling clays, and the sandy member, consisting of oil sand intercalated with clays, makes its appearance in the

lower third of the bed. The total thickness of this sandy zone is nowhere more than 30 ft. It is closely related to the line of the oil seepages. In the eastern part of the plot only this bed comes to the surface ; as we go to the west it disappears, being presumably buried under the overlying Green Clay formation.

This bed has been identified in Well No. 1, resting on Cretaceous sediments. On the north side of the Cretaceous outcrops the bed does not appear, being presumably here again buried under green clays which rest unconformably on the Cretaceous slope.

For the reasons given a few minutes ago this bed has been tentatively classed as St. Croix. The writer feels somewhat unhappy about this classification, however, mainly because were it considered merely as an oil-stained variant of the Green Clays, as G. G. Sara had it in his mapping, it would connect with them in a simple anticlinal structure, and the whole problem thereby definitely simplified. The fauna of the bed is similar in many respects to that of the green clays, but Mr. Jarvis gives as his opinion that the bed is considerably older than the Green Clay formation. The fact that this bed is oil-saturated, whilst the green clay north of the Cretaceous outcrop is absolutely free from oil, seems a potent argument against equivalent age. If it is older than the green clay, then either it or the former must have attained its position of resting on the Cretaceous by faulting, as one can hardly conceive such a violent unconformity in so short a distance. This will be touched on again when discussing the structure.

Cretaceous Rocks.

In between the last-mentioned group of clays and the Green Clays lies a belt of light grey oil-smelling clays and silty clays carrying the Upper Cretaceous fauna described to us by Mr. Jarvis. On the surface this belt can be traced for a distance of 4500 ft. along the strike, and it attains on the surface a maximum width of 300 ft. In Well No. 1 clays carrying a similar fauna were encountered at 680 ft., in No. 2 at 500 ft., in Well B at 350 ft., in A at 170 ft. Well C started in and continued in it to the bottom of the hole at 155 ft. Its certain maximum thickness in wells so far has been disclosed in Well No. 1, which cut it at 650 ft. and remained in it to the bottom of the well at 1200 ft. On the assumption of a dip of 60°, this represents a stratigraphical thickness of 260 ft.

Although the lithological characteristics of these clays do not compare well with those of known Upper Cretaceous formations in Trinidad, the assemblages of forams washed out from them lead the writer to place them in the Upper Cretaceous, because they so closely agree with those found in the Hobson clay or Tarouba shale of San Fernando and the Velasco shales in Mexico.

An authority for assigning the Velasco shales of Mexico to the Cretaceous age is Prof. J. A. Cushman, and he has given his opinion that both the Hobson's clay of San Fernando and the clays received from Lizard Springs are of the same age as the Velasco shales.

Another authority for placing the Velasco shales, on which our correlation rests, in the Upper Cretaceous is Maynard R. White in a paper published in the American Journal of Palæontology on "Index Foraminifera of the Tampico Embayment of Mexico."

Support is also afforded by our discovery of a somewhat similar, though poorer, assemblage containing the foram *Rzehakina epigona* at 9¾ miles from Sangre Grande on the Cunapo-Southern Road. Reference to Waring's map shows that he places the formation here as Cretaceous.

Waring, on page 44 of his paper, "Geology of Trinidad," says of G. D. Harris, who wrote, "Notes on the Palæontology." "Harris regards the Tarouba shale as probably Cretaceous instead of Eocene."

The foregoing considerations have led the writer to place this belt at Lizard Springs tentatively in the Cretaceous.

Structure.

The Lizard Springs Anticline occurs on the line of the Marac-Rock Dome Singineau uplifts, and was doubtless caused by the same movements. The surface attitude of all beds shows them to be dipping very steeply, both to the North and to the South, it being rare to find a dip of less than 50°. In many cases the dips are vertical. In attempting to work out the structure, dips have been treated freely, and divided into groups, which indicate the general trend of folding rather than being rigidly adhered to and so taken to represent minor puckering which is of little or no importance. Surface creep is evident within the area.

The structure consists, briefly, of a major truncated anticline, which exposes a superficial width, measured across the strike, of some 1600 to 2500 ft. of pre-Moruga rocks, flanked on the North and on the South by rocks of the Moruga formation. The strike of the pre-Moruga rocks averages about 25° North of East, while the strike of the flanking Morugas is more nearly East and West. This would seem to be evidence of two distinct periods of folding; one occurring after Naparima times (Lower Middle Miocene) and a much later and stronger one towards the end of the Pliocene. Before the deposition of the Moruga sands the pre-Moruga rocks were probably uplifted and eroded. Subsidence then set in, and the Morugas were deposited upon an eroded surface. Evidence of this partial erosion before the Morugas were laid down lies in the fact that the Morugas are found resting on both the Naparima and

the supposed St. Croix formations. This could, of course, be explained by differential sinking due to the great pressure of the overlying Morugas, and the probability is that it is due to a combination of both causes.

The area is cut into eight blocks by seven transverse faults running roughly N.N.W. to S.S.E. at right angle to the axis of the folding of the Naparima rocks. These faults were possibly caused by the later folding tending to twist the earlier folds. The effect is that the anticline is cut into a number of separate blocks, which cause rocks of quite different ages to come into contact along the faults.

The appearance of Cretaceous beds at the surface in such close proximity to Naparima and Moruga beds can also naturally be explained by unconformity, upthrust faulting, or both, and intrusion of the Cretaceous rocks into the Naparima area.

If upthrusting were the cause, the plane of division between Cretaceous and Naparima rocks should also be the plane of the fault along which the Cretaceous rocks moved up. If the movements causing this upheaval acted from the North, as is generally accepted for Trinidad, the plane along which the Cretaceous beds moved should dip towards the North. It is seen on the section, however, that the contact plane between Cretaceous and younger rocks dips to the South. If thrust faulting acting from the North is the explanation, then the Southern edge of the upthrust block should lie below and to the South of us, and should we penetrate it we should find ourselves again in post-Cretaceous formations. In other words, the Cretaceous formations we have met in our wells is merely the nose of the upheaved block ; we have yet to strike its walls.

Several geologists have in the past predicted that in drilling to the South of Well A, only Moruga rocks and possibly migrated oil would be found, but such has not proved to be the case.

Oil Seepages.

The line of oil and gas seepages in the district, about 500 ft. in length, has roughly the same bearing as the strike of the pre-Moruga beds, and they occur on the crest of the anticline, which brought the sandy beds, which has been tentatively called St. Croix, to the surface. Where these beds become buried under the green clay formation, the seepages cease to exist. The oil and gas in them would seem therefore either to have their origin in the St. Croix beds, or to have come from a deeper horizon.

Oil Occurrences in Wells.

Calyx Well A entered Cretaceous beds at 170 ft. and got its first good show of oil at 270 ft. It remained in Cretaceous beds until 585 ft. No sand whatever was reported from the well. This well was completed before the writer's arrival on the property.

Well No. 1, the next drilled, started in the Morugas, passed through the so-called St. Croix, which contained a zone carrying chert and quartzite pebbles, and entered Cretaceous beds at 680 ft. An oil zone was entered at 760 ft., which persisted on and off until 845 ft. While there was a certain amount of oil sand associated with the beds immediately above 680 ft., in the oil zone no sand whatever was passed through. Core samples, however, showed up the presence of several thin shattered clay zones, which tallied with increased flows of oil.

Calyx B, South of Well No. 1, was started in Morugas and remained in them until 350 ft., when it suddenly encountered Cretaceous clays without the St. Croix beds having been met with at all. The well was carried to 650 ft. Between 350 ft. and 650 ft. a thin bed was entered, which carried a similar fauna to the alleged St. Croix and the well finished in Cretaceous formation.

Well No. 2, offset 300 ft. Westwards along the strike, entered Cretaceous clays at 500 ft., and cut an oil zone at 885 ft. to 945 ft., in which the same conditions of shattering obtained as were observed in Well No. 1. No sand was recorded. The well was carried to 1100 ft. without further oil signs, the formation carrying a Cretaceous fauna from 500 ft. to 1100 ft.

Analysis of Lizard Springs Crude.

The Analysis of Lizard Springs Crude has been kindly supplied by Mr. D. M. Walsh, who writes :—

Average Production sample from Wells 1 *and* 2.

Tests.

Colour			Dark Green.	
Water (by distillation)			Nil.	
Sp. Gravity @ 60° F.			0·815	
I.P.T. distillation.				
I.B.P. 95° C.				
Distillate up to 150° C.		32·0%	Sp. Gr. @ 60° F.	= 0·771
Distillate up to 150°/300°		56·5%	,, ,,	= 0·822
Residue		10·5%	,, ,,	= 0·903
Loss		1·0%		

Residue remained fluid at 6° F. and has a viscosity of machine oil at ordinary temperature.

Light Crude in Well 2*a at* 880 *ft.*

Tests.

Colour			Dark Green.	
Water (by distillation)			Nil.	
Sp. Gravity @ 60° F.			·798	
I.P.T. distillation.				
I.B.P. 95° C.				
Distillate up to 150° C.		46·0%	Sp. Gr. @ 60° F.	= 0·769
Distillate up to 150°/300° C.		49·0%	,, ,,	= 0·811
Residue		4·5%	,, ,,	= 0·905
Distillation loss		0·5%		

Residue remained fluid 6° F.

Age of the Oil.

Turning to the question of the probable age of Lizard Springs oil, many geologists hold that it is of St. Croix age. The section shows that all oil which has flowed into Lizard Springs wells has been struck in formations considered to be Cretaceous. It has also been mentioned that where oil has been struck, it has been in shattered formation. It has also been shown that these shattered zones containing oil lie at different distances below the top of the Cretaceous beds. In Well No. 1 40 ft., in Well No. 6 50 ft., and in Well No. 2 193 ft. stratigraphically below this plane.

This seems to lead to the conclusion either (*a*) That the oil is of Tertiary age, and, lacking a suitable reservoir within Tertiary beds has found one in fault zones in the Cretaceous or (*b*) that the oil is of Cretaceous origin.

By reason of the fact that no sandy beds at all were found in the Cretaceous in the wells referred to, and that below the oil zones the Cretaceous silts and clays appeared non-petroliferous, the oil, if it is Cretaceous, must have migrated upwards through fault zones from sources deeper than those penetrated in the Lizard Springs wells.

An article in a recent issue of the *Petroleum Times* gave an account of an oilfield in Ecuador where Tertiary oil found a lodgment in the fault zones of underlying Cretaceous rocks.

This paper is being read by kind permission of the management of the Trinidad Central Oilfields, Limited.

DISCUSSION.

Mr. C. A. P. Southwell said that it was rarely that two geologists agreed on every point, and that, with regard to the area in question (which was complicated and a difficult one to interpret) it was doubtful whether an agreement could be arrived at.

Mr. Skelton had omitted one controversial point in his paper. It was, perhaps, done in order to stimulate argument, but he had come there that evening in the belief that Mr. Skelton would take up this controversial point of mud flow breccias and stamp on it with a weight of argument and fact. It is a point which has created great interest in the geological study of the island :—" Are the Cretaceous rocks found in certain parts of the island due to mud flow ? "

It is also possible that the position of the Cretaceous was due to faulting more than to the question of unconformity. The author of the paper mentioned faulting, but only dip faulting of the block faulting type, and not thrusting or over-riding of different horizons.

He would like to ask Mr. Skelton if any evidence of mud flow had been obtained, and if Mr. Skelton appreciated how large a block of Cretaceous could be carried up in a fault breccia.

There are two main sides of the paper read :—First, the foraminiferal aspect provided by Mr. Jarvis, who is a real enthusiast in the study of foraminifera and knows more about the local foraminifera than anyone else. He is the only man who has given any considerable time to this scientific study. On the other hand we have the tectonics and stratigraphy interpreted by Mr. Skelton, using the foraminiferal evidence provided by Mr. Jarvis. We have, therefore, to take Mr. Jarvis' evidence based on Cushman as being a fact that Cretaceous fossils are present. On the other hand the question of the tectonics and stratigraphy are open to argument.

From the point of view of mud flow or fault breciation there was the additional evidence of oil. The oil produced from the wells drilled in the areas in question was of an exceedingly high quality and indicated somewhat the presence of considerable movement. It was not the type of oil found in large and regular structures. It appeared to him that, if the oil were indigenous to the Cretaceous rocks it would have all evaporated with the Cretaceous rocks at the surface, as the oil was so light and would evaporate off one's hand in a few minutes. He believed that the oil was a migrated oil from younger formations into the fault breccia, which contain Cretaceous rocks and that, with the gradual later movement, small lenses were opened up and permitted what is one of the most remarkable seepages in Trinidad if not in the whole world.

He put these views forward as another side of the problem mainly as a basis of argument, and hoped that other members who had knowledge of this area would take up this argument.

Mr. G. H. Scott said he was of the opinion that the whole question as to a Cretaceous origin of the oil hinged on the question as to whether the Cretaceous beds shown as occupying the crest of the structure were truly Cretaceous or whether they were interbedded mud flows in the Moruga beds.

To the south of Lizard Springs in the Guayaguayare district and along the Kaiper structure similar beds were found which were often flexured and carried blocks of varying ages, and he believed that the concensus of opinion was that these were mud flows which were contemporaneous with the deposition of the Moruga beds. If the Cretaceous beds described by Mr. Jarvis were of similar character half of the questions as to the origin of the oil raised by Mr. Jarvis were automatically answered.

He had carried out extensive and detailed work on the Rock Dome structure which was a continuation of that of Lizard Springs

and found there very similar conditions to those described by Mr. Skelton. Thus, whereas to the north of the structure there was the normal sequence of Morne L'Enfer beds, cyclammina clay, green clay and St. Croix, to the south one passed directly from the Moruga beds to the marls of Oligocene age with no representative of the Naparima clays. The St. Croix beds on the north flank of the structure were represented by the so-called Herrera sands which were typical passage beds and whose character typically exemplified unconformable conditions of deposition. Similarly to the south the base of the Moruga beds was often marked by boulder beds carrying hard, well-rounded quartzitic cobbles up to 1 in. in diameter and isolated lenses of *amphistegina* limestone were also found. Now this *amphistegina* limestone, identical with that found at Brigand Hill, is considered to be also of St. Croix age, so that there is very definite evidence for a great change in the nature of the deposition to the north and south of the old southern horst; and while the Naparima clays were being laid down to the north, the shallow water Moruga phase still persisted to the South.

He brought up this point as if similar conditions existed in the Lizard Springs area, and such was indicated by Mr. Skelton; the whole conception of the structure was greatly simplified. They had not to worry about an extensive thrust fault cutting out the Naparima clays to the south, as the Naparima clays would never have been present there, and in this case the oil would seem to be derived from the basal Moruga beds which he posulated might be of St. Croix age.

This great change in the nature of the deposition in the northern and southern basins must mean that they were separated by an old land surface, and the criticism might be advanced that there was no evidence for its existence there. If, however, the Cretaceous beds were actually *in situ* they would have constituted the necessary bar to the uninterrupted deposition, and even if of mud flow origin the large quantity of included blocks of Cretaceous age points to the fact that the Cretaceous beds were at no great distance from the surface.

He understood Mr. Harris to say that San Fernando Hill was oil soaked, but a careful examination would show that this was not the case, as the oil only existed in the fracture and joint planes in the argiline and probably owed its origin to an upward migration from the clays underlying the thrust plane, it being generally admitted that the San Fernando argiline is a portion of an overthrust sheet.

He fully subscribed to what Mr. Southwell said. They should take the simplest origin for the oil and one entailing no tremendous

upward migration. The Naparima clays and the marls underlying them contained the necessary organic matter for the formation of oil and no fantastic migration to the reservoir rocks was involved.

Mr. A. J. R. Murray said, on the question as to whether oil was indigenous to the Tertiary or whether it was indigenous to the Cretaceous, it might well be indigenous to both. Oil does occur in beds of both ages, but he was of the opinion that it is indigenous to the Tertiary so far as Trinidad and the Northern Republics of South America are concerned.

In Venezuela, north-west of Maturin and south of Barcelona in the Estado de Anzoategui, he had seen in the foothills of the Northern Range seepages of petroleum in the Cretaceous formation; these occur at the junction of the Cretaceous with the Tertiary.

He said that it was presumed that the oil had migrated downwards from the Tertiary, although in the region seen by him there was no evidence to prove that oil was present in the younger beds.

In Colombia similar conditions appertain to the foothills of the Eastern Range of the Andes, which is a part of the same Cordillera as the Northern Range of Venezuela Three hundred miles up the Rio Magdalena to the Port of Gamarra and in east from there, one encounters a faulted junction of the Cretaceous with the Tertiary; seepages in the Cretaceous are plentiful and continue to be so along this line for at least sixty miles south.

Oil has been encountered in wells drilled into the Tertiary, but not in those drilled into the Cretaceous; the presumption is again that the oil is indigenous to the Tertiary and has migrated to the older formation.

Going across to the West of Columbia to the Rio Sinu, which is between the Central and Western Cordilleras of the Andes, there are good shows of light oil seeping up through vertical beds of questionable Cretaceous age; it is possible that these beds were of Eocene age, but the point at which these seeps were observed was a long way in from the contact of this series with the Miocene. He was of the opinion that this oil was indigenous to the formation from which it is seeped, but whether this was Cretaceous or Eocene could not be proved for lack of fossil evidence; this was the only case seen by him where there is a possibility of Cretaceous oil occurring in the Northern Republics of South America. And that is a meagre one.

In North-Western Peru, up the Quebrada Parinas, may be seen the basal conglomerate of the Eocene on one side of the valley and the Cretaceous beds which have a distinct smell of petroleum on the other. But there is no evidence of oil being indigenous to the Cretaceous, while it is known to be Tertiary.

In a recent article in the *Petroleum Times* Mr. Cunningham Craig stated that he had visited the Santa Elena Peninsular, Ecuador, in 1920, and was of the opinion that the oil had migrated down from the shattered Tertiary beds into the underlying Cretaceous. The speaker has done considerable work there, and is of the opinion that the beds are not Cretaceous but Tertiary; they have been intruded by a basic magma which has altered them by the process of hydro-thermal metaphorism. The oil found in these beds is indigenous to them, but as a result of the heat to which they have been subjected, the oil has become inspissated and it is so heavy that it is mined from hand-dug pits which may be up to 80 ft. in depth.

Wells drilled in this series have encountered both very heavy and very light oil, the latter having been retorted as a result of the igneous intrusions.

He disagreed with Mr. Cunningham Craig that the rocks were Cretaceous, but he said that Cretaceous rocks did exist elsewhere in Ecuador. From what he had seen in Venezuela, Colombia, Ecuador and Peru, with the exception of one questionable area in Western Colombia, he did not think oil was indigenous to the Cretaceous in either Trinidad or the Northern countries of South America, and he would suggest that in Lizard Springs the oil found in the Cretaceous was the result of migration.

Mr. H. G. Busk, in answer to the question of the author, said that oil-bearing Cretaceous beds were existent in Venezuela.

Mr. P. W. Jarvis, replying to an inquiry if the Cretaceous material at Lizard Springs could be accounted for by a mud-flow from the lower beds, said there were no signs of any such disturbance there and from the fact of the fossils being all Cretaceous (none of other ages) and in such perfect condition, they must be considered to be *in situ*. The mud-flow at Guayaguayare did not resemble this bed, the samples examined were unfossiliferous.

In reply to a statement that the oil found at Fyzabad most likely originated in the "Cruse beds" directly under the Forest Clay series, Mr. Jarvis said it was highly improbable that "Cruse beds" were the source, as surface exposures of these beds were unpetroliferous. Prof. Illing some years ago made extensive and careful search for oil in these "Cruse beds," but failed to discover it.

The Chairman moved that a vote of thanks be accorded the Leaseholds for the use of their room and Messrs. Skelton and Jarvis for the interesting papers they had read. This was carried with acclamation and the meeting closed.

The following has been received from Mr. E. H. Cunningham Craig :—

These two papers, with the discussion, raise not only an important point with regard to the geology of Trinidad, but also have some bearing upon South American problems. A few remarks may therefore be permitted to the writer, who was the first to examine the Lizard Springs area with the view of ascertaining the ages and structures of the various strata and the possibility of petroleum production. There is no doubt about the presence of Cretaceous rocks at Lizard Springs.

When I visited the ground first about the end of 1903 I suspected that some of the strata were of Cretaceous age, but found no fossils to confirm that theory. Later, after further work on the Cretaceous formation, and especially the study of specimens from one of the Guayaguayare wells, I was convinced that my view was correct, but owing to illness I was not able to return to the ground to map the Cretaceous outcrop. There is a much greater area of Cretaceous rocks in Trinidad than many geologists suspect.

That formation in Trinidad is generally folded on N.E. to S.W. axes and is apt to form solid ridges at right angles to that direction. The post-Tertiary movement acting obliquely to these ridges develops some interesting structures in the Tertiary rocks—*e.g.*, the step faults of the Cunapo "coalfield," which seem to have considerable horizontal displacements along vertical dislocation planes. The faults of the Lizard Springs area may be somewhat similar.

I doubt the presence of anything approaching a thrust plane, but unconformability and overlap of the Tertiaries on the Cretaceous are obvious.

As regards the question of petroleum of Cretaceous age in Trinidad, I have never found any evidence of it, though I know of several localities, and more than one well, which give or have given good shows or small productions of filtered oil from Cretaceous strata. Such oils are similar to the Lizard Springs oils.

In some parts of both Venezuela and Colombia I believe there may be petroleum indigenous to the Cretaceous, though I know of no actual proof of this having been published.

In the coastal region of Ecuador the impregnated Cretaceous Oceanic rocks, which have been mistaken occasionally for altered Tertiaries, are overlaid with a violent unconformability by the Lower Tertiaries, and have suffered from earth movements that do not affect the Tertiaries. The impregnation with petroleum is only observed in the vicinity of oil-bearing Tertiary strata.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

South Wales Branch.

On Monday, May 6, 1929, the new South Wales Branch of the Institution held its inaugural meeting at Llandarcy.

Dr. Dunstan, President of the parent body, was present, and in addition to Mr. W. C. Mitchell, the branch chairman, the members were fortunate in having the company of Mr. W. E. Aylwin, President of the Abadan Branch.

About forty-five members of the staff of the National Oil Refineries Ltd., were present, and after tea the meeting was opened by a few words from the Chairman, who explained the purpose and hopes of the committee in forming the branch.

Dr. Dunstan followed with a very interesting account of his recent tour in the States, giving a brief outline of the present practice of petroleum refining there. He also encouraged the members in following what he considered to be the thoroughly British practice of joining or if necessary forming a society in which the professional matters could be discussed and personal contact made.

Among other points he stressed the great future of oil and oil technology.

The Chairman in a few well-chosen words recalled his speech at the opening of the Abadan Branch and asked Mr. Aylwin to convey to the sister society in Persia their best wishes.

Mr. Aylwin described the difficulties which had been successfully overcome in forming a branch in the desert, and concluded with some sound advice based on his own experience.

The summer will be spent in laying foundations for what it is hoped will be a good winter session.

Conditions Encountered in Foreign Fields: Rumania*

By Lewis McL. Drader, M.A.P.I. (Member).

The United States of America, in which the Petroleum Industry, as known to-day, first started, and which at present produces about 68 per cent. of the total world's production of crude oil, as well as possibly about the same percentage of all oil-country equipment, can well be taken as a standard with which to compare other fields. The term "foreign fields" will, therefore, imply those fields outside of the U.S.A.

The subject of the conditions and difficulties encountered in any particular oilfield is too vast to be dealt with in detail in a short article, but the author has endeavoured to deal with the matter in a general sense, including both the administrative and the technical phases. As far as possible all personal themes and theories have been avoided.

In the present article it is proposed to deal with Rumania and to discuss the typical difficulties met with in the operations of an oil company in that country. Every field, be it in whatever country, has its own drilling and other technical problems which cannot all be discussed and must be merely touched upon.

Mining Laws and Regulations.

All oil companies must have at their field offices a map, showing the location of all derricks, buildings, and installations of every kind and description, which may be inspected whenever necessary by the mining officials of the Government. This plan must be sent to the authorities at the beginning of every year, and may only be made by a fully qualified mining engineer or a topographer specially licensed by the Government.

In the same way proper registers and report books must be kept at all offices, showing strata passed through, casing utilised, accidents and fishing jobs, details of water met with and shut off, production from all wells, fires, etc.

Daily drilling logs or profiles, of a type laid down by the authorities, must be kept up, and cores or samples must also be filed away.

All managers, engineers, head-drillers, drillers and specialists in any branch must be properly qualified through passing the examinations held by the Government, and must show diplomas and papers whenever required. A list of these must be forwarded at stated intervals to the Mining authorities.

* Paper received April 4th, 1929.

Wells must not be drilled closer than 30 metres to a boundary line, nor closer than 20 metres to classified roads, whereas the distance between wells is fixed at not less than 60 metres. Oil tanks of over 300 cubic metres capacity must be at a distance of from 40 to 50 metres, depending upon size. Open fires may not be closer than 40 metres to a well and boilers may not be over the 20 metre line.

Companies are obliged to commence drilling operations within two months from the time the drilling authorisation is received, otherwise the permit to drill becomes null and void.

Regulations are in force respecting doors and windows of derrick and rig, ladders, platforms and crown-blocks, dividing off of engines, motors, pumps, etc., from the main body of the rig, boiler-houses, methods of bailing, tanks of various descriptions, pipe-lines, electric installations, etc.

Assuming that the necessary lands have been acquired and that the company to operate them has been organised, the first step is the location of the wells to be drilled. This is the work of the company's geologist. As any oil-man knows, no absolute certainty of the value of lands acquired can be ascertained until after a well is drilled. A small plot of land in a proven district may turn out to be absolutely worthless, whereas a similar piece in an uncertain position may produce a big well. A large acreage, which has good producers on more than one side, rarely fails, however, to give results, but whether good or indifferent, cannot be forseen. The estimated chances for success govern the price paid for lands, and the true value of a company's holdings cannot be estimated until several wells have been sunk.

Managing Staff and Labour.

In order to comply with the Rumanian laws, it is necessary that the responsible superintendent or manager should be a fully qualified mining engineer, authorised by the Government to function as such. In most cases this "Sef de Exploatare" is a Rumanian, and it is necessary that many other staff positions be held by persons of Rumanian nationality. The effect is that a number of the company officials are duplicated, the Rumanian being nominally in charge and responsible for the carrying out of the various legal operations, while the foreigner is actually in charge of operations.

The Sef de Exploatare is responsible for all accidents and fires and any infringements by the company or its representatives against the rules and regulations, and must also sign for the company in and for all technical matters. Some foreigners possess their Sef de Ex. papers, but many foreign companies find it advan-

tageous to duplicate this position and divide up the duties, as explained in the previous paragraph.

For the erection of buildings, etc., and for general unskilled work, only Rumanians are employed, but occasionally in the workshops Germans, Hungarians, Poles, etc., are to be found, although only a small percentage of foreign labour may be utilised. The actual drilling of the wells is done entirely by Rumanian labour, supervised by both Rumanian and foreign engineers.

The Rumanian peasant employed in the oilfields is as a general rule very patient, and although not exceptionally efficient, is by no means lazy although appearing to be so by reason of his slow movements.

Some of the large companies employ "practicants," *i.e.*, men who work for the first year at a nominal salary, receiving a substantial increase in the following year if satisfactory. After three or four years practical experience, lease superintendents are chosen from these men. In one company here in Rumania only men holding a B.Sc. (Technical) are engaged as "practicants." This system works well if the practicant takes naturally to the oil business, and has the added advantage of producing practical oil men with a good education.

As in other countries, a large proportion of oilfield work can be done more cheaply and efficiently, if properly supervised, by contract, as the best labour is generally obtained by the contractor, who pays better wages than the average company.

Drilling Systems and Equipment.

Although some companies import most of their equipment, it is the usual custom to purchase second-hand material which is available in the country. This second-hand material is much cheaper than the new and answers the same purpose, particularly where the company has good workshops and can carry out necessary alterations and repairs.

Practically all methods of drilling have been tried in Rumania, and at present, to the writer's knowledge, eight systems are in use in the country. The majority of the wells have been drilled by the Canadian system, which has now been modified to use a wire-line in place of poles and in some cases also uses the Cable-tool "bull-wheels." Although this method usually drills a straight hole and casing is easily carried by reason of the eccentric bit used, the main disadvantage is its slowness; under ideal conditions a hole drilled by this system can be carried down to seven or eight hundred metres in about ten months; this depth, however, is

reached, under average conditions, in upwards of one and a half years owing to fishing jobs, water shut-offs, casing troubles, etc.

The Cable-tool system is used by very few companies as many Europeans claim that "flat" holes are more common with this method than with the Canadian. The average drilling speed of the Cable system in Rumania is 100 metres a month to a depth of about 1000 metres. This system drills much faster than the old Canadian method, being more powerful, having fewer parts to keep in repair, having a longer stroke, and last but not least fewer belts to keep in order.

The Rotary system is becoming increasingly popular in Rumania, and has broken all speed records in the country. The system has still many enemies who firmly believe and maintain that slanting and crooked holes are the rule without exception, and that all surrounding sands are invariably flooded with water and mud by rotaries. Needless to say this opinion is slowly being swept away and many regulations previously in force, which adversely affected the Rotary system, have been done away with.

Speed is the Rotary's chief advantage over other systems ; this, however, is not everything and would-be record wells which end in long disastrous fishing jobs, sometimes meaning the abandonment of the well, are not by any means the exception. Speed in drilling requires a number of conditions not always found together ; chief among these are : good material, good administration, drillers above the average, speed in transportation, very short shut-downs, if any, and fishing jobs of a very short duration.

Given all these factors a rotary hole can be drilled to 1000 metres in Rumania in about two months, rarely faster, although the time taken to reach this depth is generally six months or over, due to the usual delays and shut-downs. Over 1500 metres is now being reached in Rumania with the Rotary, where 1000 metres was previously the exception.

In addition to the systems mentioned above, a number of German or Austrian methods, using circulation and various types of walking beam, are employed, and several types of modified rotaries are also in use.

Very few rock-bits are in use in Rumania and the systematic use of core-barrels has only recently commenced. Spring hooks are used almost everywhere, but rotary under-reamers and rotary jars are ultra-modern. Automatic cat-heads, weight-indicators, drilling charts, and the Halliburton and other drilling controls are to be found in a few places.

Derricks are generally of wood, although some steel ones are found here and there, and one company uses only the latter kind, of their own manufacture and made near Ploesti. Derricks, sump-

holes, tanks, etc., are usually made or erected more quickly by contract, meaning, of course, a time clause, proper supervision and no loss of time in obtaining material.

In obtaining drilling equipment, the all-important factor is a good set of fishing tools. Fishing tools, in Rumania, where material and equipment is not obtained at a moment's notice as in the U.S.A., must be plentiful, of all varieties, and if possible of the latest models if time is to be saved and the loss of a hole avoided. If the right tool is not at, or close to, the rig, sand may settle around and above the lost article before a tool can be obtained.

Casing is nearly all inserted-joint, collar casing now being the exception. Until recently all casing was handled with clamps or swivels, making the running in of a long string a lengthy operation. The introduction of elevators for inserted-joint casing has considerably lessened the time required to lower a string of casing.

Cementing methods for setting casing are not in favour with old drillers, who are accustomed to driving casing into a clay formation to effect a water shut-off. It has been suggested that some standard make of cement should be introduced into Rumania, agreed upon by all companies, as at the present many failures in cementing are attributed to the cement used.

Air- and gas-lift are very new in Rumania, and have at present not been sufficiently tested to make any opinion worth while. Several short articles on this subject have already been written—nevertheless, the time is not opportune to discuss the matter, as data regarding air- and gas-lift in Rumania is both scarce and confusing.

Steam power is being slowly replaced by both crude oil and petrol motors and also gas engines, but the cost of electricity frequently makes electric motors prohibitive.

Bringing the Oil to the Surface.

The majority of the wells are bailed, various types of bailing machines being employed. This is possible owing to the cheapness of labour in the country, which is, however, becoming slowly but surely higher and higher in price. Stabilisation of the "Leu" may mean some standard in this respect in the future; heretofore regular increases in salary from practically month to month were the recognised custom.

Flowing wells exist, but are the exception, whereas pumping wells are found only in the old fields. Air- and gas-lift, as already mentioned in this paper, are in the experimental stage.

Transport.

This is one of the greatest problems in the petroleum industry in Rumania. Roads in Rumania are notably bad for at least the

winter months, and in summer heavy dust replaces the deep mud of the winter. Wells being more often in the most inaccessible spot in a given district, good roads are imperative but too costly to build under present conditions.

A few years ago a paved main road was started from Bucharest towards Transylvania, but only a few short patches have been completed, totalling about 80 miles in all perhaps. If finished, a portion of this road, which runs through Ploesti (the capital of the Rumanian Oil Country) with branches to the main oilfields, would be constantly in use by the oil companies. The portion between Baicoi and Moreni, which is not on the main road, has been finished and is in use.

The greater part of transportation in Rumania is carried out by means of oxen and horses, as many as sixteen to twenty pair of oxen sometimes being required for one load, but very recently fleets of lorries and heavy motor vehicles have been put on the roads.

The railways of Rumania are government owned, although the matter of giving concessions for railroads to a number of foreign firms has been frequently projected, in particular within the last year. The two best routes into the country are via the "Orient" or the "Simplon" expresses, the former travelling through Vienna and the latter through Switzerland.

Within the last two or three years omnibus services have begun to appear on the main roads; these are usually privately owned, most owners having only one vehicle. The tax on cars and motor vehicles has, however, risen enormously this year, and this will probably tend to be the means of placing better and heavier omnibuses on the roads.

A new pipe-line to the sea has been projected, but the question of the necessary capital presents certain difficulties. The subject of this pipe-line has been put forward again recently and there is every possibility of the handling of petroleum being facilitated in the near future.

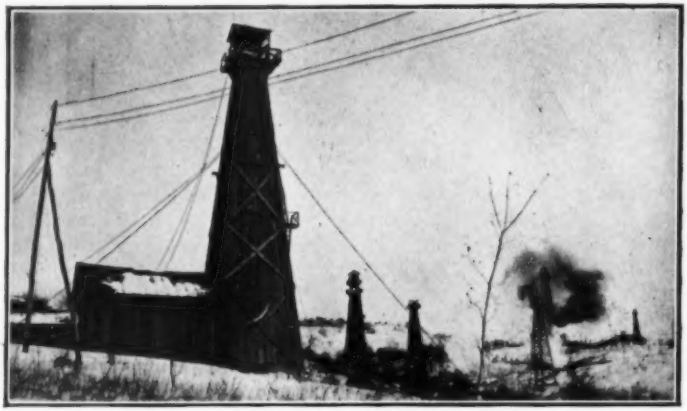
Living Conditions.

Generally speaking, living conditions in Rumania are comfortable, as compared with many other foreign fields. However, the cost of living is high, having risen enormously in the last five years, and is still increasing, although the recent stabilization of the currency will naturally tend to finally bring prices to normal levels. Bargaining is the rule almost everywhere but in this respect matters are improving from day to day.

At the present time prices fluctuate greatly, except as regards a few staples, among which salt, tobacco and matches are state monopolies. Rumania is very poor in manufacturing concerns

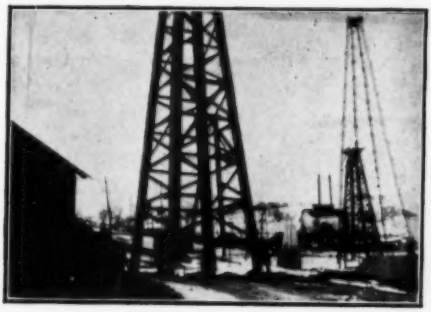
A WINTER SCENE IN RUMANIA.

A ROTARY RIG IN RUMANIA.



A CANADIAN RIG IN RUMANIA.

A CABLE TOOL RIG IN RUMANIA.



Standing.

Falling.

On the ground.

DISMANTLING A CANADIAN DERRICK IN RUMANIA.

A BURNING WELL IN RUMANIA.

A WELL BEGINNING TO FLOW.

THE MORENI FIRE, 1929.

View taken when the fire started, showing several wells burning and tanks, sump-holes, etc., on fire.

THE MORENI FIRE, 1929.

View showing the gas alone burning at the original well which caught fire.

and imported articles are heavily taxed, which is one of the causes of the high cost of living.

Quarters, as a general rule, are not much of a difficulty, as most oilmen have houses supplied by the companies, both at headquarters and on the leases.

Rumania has a climate of extremes, winter frequently resembling Siberia and summer being almost semi-tropic in intensity, although sunstroke is very uncommon.

Maize is the chief product of the soil, the peasants eating chiefly a food composed of corn-meal; wheat, barley and oats are also grown in big quantities, the soil being very fertile. Grape-vines are plentiful and wine is cheap.

Language.

Many a newcomer to Rumania is greatly handicapped by a lack of knowledge of foreign languages, and one who has already had a grounding in two or three languages in his earlier education is lucky indeed. French is spoken by all educated Rumanians and in business German is very common; English is being taken up by the present generation, although a very small percentage now speak it compared to those who understand French and German.

A knowledge of the Rumanian language is a great asset, as otherwise all conversation must be carried on through an interpreter, with consequent confusion on both sides, unless care is taken to see that all orders are properly understood. Those who do not take the trouble to learn the language of the country are invariably hoodwinked for years, a fact which is universal for all countries.

General.

The richest accumulations of oil in Rumania are invariably found close to domes and beds of salts. Traces of oil are found from the Pliocene down into the Lower Cretaceous, but in commercial quantities oil is being extracted almost entirely from the Pliocene. In the latter division or system the chief production is from the Dacic and Meotic sands, although oil exists also in the Levantic and Pontic.

Previously oil was produced chiefly from the Dacic sands (Pliocene), hand-wells having been dug to depths of several hundred metres many years before the advent of the drilling rig. The "Drader" sand in the Dacic has been very prolific but is playing out. The third sand in the Meotic (Pliocene) has recently been drilled through in Moreni and the tendency is to find deeper production as the upper sands are exhausted and water-logged.

Rumania's biggest production has been from the Moreni, Ochiuri and Gura Ocnitei fields. One of the newest fields has been Cheptura and just at present Chiciura is being intensively exploited.

It is calculated that Rumania has a total extent of 100,000 hectares of commercial oil-producing territory, of which some 60,000 hectares have already been taken up by oil companies. Of these almost 2,000 hectares are State property. Only some 4,000 hectares odd are at present producing oil.

While the future of Rumania from the point of view of the petroleum industry is very promising, the present laws governing the winning of crude oil impose restrictions which are not in favour of the exploitation of petroleum producing territory by other than Rumanian nationals.

However much prophesying and prospecting may or may not be done as to the value of possible oil territory and as to the playing out of present oilfields, the fact still remains that huge stores of oil are at present untouched and that oil will be found in Rumania, as in other countries, in regions undreamed of and unknown. The wild-cat well, as of yore, will now and then open up a new field and the man or the company with the necessary courage and breadth of vision will reap his reward in big production, to-morrow as he did yesterday.

Methods of Quantitative Determination of Aromatic Hydrocarbons in Gasolines Produced by Straight Distillation.*

By M. D. Tilitsheyew and A. I. Dumskaya.

I. Introduction.

The importance assumed at present by the question of quantitative determination of aromatic hydrocarbons in gasolines creates further tendencies towards improving the accuracy of the existing methods.

The most accurate and generally recognised methods of quantitative analysis for aromatic hydrocarbons are those based on the determination of certain constants pertaining to gasoline before and after the separation of aromatics by means of sulphuric acid.

In general cases the determination of aromatic hydrocarbons is done by means of the following formula:

$$x = k.\ d.$$ [1]

Where x is the percentage of aromatic hydrocarbons by weight; d the difference between the gasoline-constants before and after the separation of aromatics and k is a co-efficient, which is obtained by experiment.

The principal constants, which may be used for the purpose of quantitative determination of aromatics, are the following: the Critical Solution Temperature of gasoline in various liquids (on which are based the aniline, nitrobenzene and similar methods), the Specific Gravity and the Refractive Index.

The values of the co-efficient k for each of the four methods mentioned generally depend upon the following factors:

1. The nature of aromatic hydrocarbons.
2. Fractional composition of gasoline.
3. Chemical composition of the non-aromatic portion of gasoline or narrow fraction[2] under test.
4. Concentration of aromatic hydrocarbons.

The influence of the first two of the above factors can be practically eliminated by means of redistilling the gasoline into narrow

---

* Paper received May 29th, 1929.

[1] The above formula assumes the co-efficient k to be independent of the degree of concentration of aromatic hydrocarbons. However, as we shall see later, the value of this co-efficient depends to a certain extent upon the concentration. Therefore, the above formula may be only used for narrow limits of concentration of an aromatic hydrocarbon, and for each phase of concentration (for instance, from 0 per cent. to 10 per cent., from 10 per cent. to 20 per cent., etc.) there is a separate co-efficient.

[2] Under the "non-aromatic portion" of gasoline or fraction will be further understood the mixture of paraffin and naphthene hydrocarbons, which remains after the extraction of aromatics.

fractions—corresponding either to the individual or nearly similar in composition aromatic hydrocarbons, the fractions being as follows:

1. 60°—95° C. (benzene fraction);
2. 95°—122° C. (toluene fraction);
3. 122°—150° C. (xylene fraction), and
4. 150°—200° C.,

and the aromatic hydrocarbons are determined independently in each respective fraction.

Such, for instance, is the method described in the "Standard Methods of Testing Petroleum and its Products," 1924,[3] where the co-efficients given for the benzene, toluene and xylene fractions are respectively: 1·15, 1·20, 1·23. These co-efficients, however, will vary in accordance with the variable composition of the non-aromatic portion of fractions. This latter fact, as was correctly mentioned by Carpenter,[4] has not been hitherto sufficiently recognised.

As the chemical composition of the non-aromatic portion of fractions is more or less accurately characterised by the constants, we can say with sufficient approximation that the values of the co-efficients are functionally dependent on the constants of the non-aromatic portion of fractions. The establishing of this functional dependence forms the main object of this paper.

Beside the aniline method, we have also investigated from this viewpoint the nitrobenzene, specific gravity and refractometric methods.

The general plan and mode of procedure adopted in these investigations were as follows:

Artificial mixtures containing 10 and 20 per cent. of aromatics were prepared from individual aromatic hydrocarbons (Benzene, Toluene, Xylene) and corresponding fractions, which were previously freed from aromatic hydrocarbons.

The 150—200° C. Fraction was mixed with Cymol, which was selected as an average representative of aromatic hydrocarbons boiling within 150—200° C.

The petroleum fractions were selected with such a consideration that their constants, after the extraction of aromatics, should vary in the widest possible limits.

The grades of petroleum most suitable for this purpose were selected without difficulty, using as guide a paper on chemical composition of petroleum by Prof. A. N. Sachanoff and R. A. Virabiantz.[5]

---

[3] Institution of Petroleum Technologists. (These co-efficients have been abandoned in the 2nd (1929) Edition of these Standard Methods.—ED.)

[4] *J. Inst. Petr. Techn.*, 1926, **12**, 545.

[5] Neftianoe Khosaistvo, No. 9, 1928.

For the preparation of artificial mixtures with aromatic hydrocarbons, beside the petroleum fractions, we have also used pure paraffin and naphthene hydrocarbons.

The basic constants—*i.e.*, the critical solution temperatures in aniline[6] and nitrobenzene, the specific gravity and the refractive index were then determined both for the petroleum-fractions (or hydrocarbons) freed from aromatics, and for their respective artificial mixtures with aromatic hydrocarbons.

By dividing the percentage of the aromatic hydrocarbon by the variation in the value of one or the other constant was found the co-efficient k, which varied in accordance with the variations of the constant of the non-aromatic portion, the nature of the aromatic hydrocarbon and its concentration.

For different solutions containing the same aromatic hydrocarbon with the same degree of concentration, the co-efficient k has become a function of only one variable, that is: its value depends entirely upon the variations of the constants of the non-aromatic portion of fraction.

By setting off on the axis of abscissæ the values of one or the other constant of the non-aromatic portion of the fraction, for instance the aniline point (critical temperature of solution in aniline), and on the axis of ordinates—the values of the co-efficient k, we have plotted for each aromatic hydrocarbon a series of points, through which was drawn a curve showing the functional dependence of the co-efficient k from the aniline point of the non-aromatic portion of fractions.

Similar curves were also obtained in connection with the remaining methods (specific gravity and refractometric).

The co-efficients k relating to the above mentioned various methods will be further referred to as:

1. Aniline co-efficient (for benzene, toluene, etc.);
2. Nitrobenzene co-efficient;
3. Specific gravity co-efficient, and
4. Refractive index co-efficient.

For the purpose of determining the aniline points a sulphate-purified aniline with a melting temperature of −6·3° C. was used.

In view of the bulkiness of the experimental material, we include here detailed data only for the aniline points of the artificial mixtures with benzene, but in the remaining instances we have limited ourselves to a final statement of co-efficients obtained from experimental data.

[6] The determination of the aniline points (further referred to as aniline points) was effected by a method described in the "Standard Methods of Testing Petroleum and its Products," 1924.

TABLE

Aniline Points of Artificial Mixtures with Benzene.

Order No.	Description of the non-aromatic portion of mixture.	Description of the aromatic hydrocarbon.	Content of aromatic hydrocarbon in % by weight.	Aniline-point in ° C.	Depression of aniline point in ° C.	Coefficient.	Depression of aniline point per 1% of aromatic.	Quantity of aniline per 1 volume of fraction.
1	65–95° Fraction, Surachany Crude treated by fuming H_2SO_4	Benzene	0·00	59·07	—	—	—	
2	Ditto	„	10·01	50·80	8·27	1·210	0·00083	
3	Ditto	„	20·17	42·25	16·82	1·199	0·00083	
4	75–85° Fraction, Grozny Crude treated by concentrated H_2SO_4	„	0·00	57·57	—	—	—	0·9
5	Ditto	„	10·08	49·21	8·36	1·206	0·00083	1·2
6	Ditto	„	9·99	49·25	8·32	1·200	0·00083	1·3
7	Ditto	„	20·02	40·74	16·83	1·189	0·00084	1·4
8	Ditto	„	20·04	40·73	16·84	1·190	0·00084	1·4
9	60–95° Fraction, Surachany Crude treated by 100% H_2SO_4	„	0·00	51·44	—	—	—	0·9
10	Ditto	„	10·02	42·80	8·64	1·159	0·00086	1·2
11	Ditto	„	20·09	34·26	17·18	1·169	0·00086	1·3
12	60–95° Fraction, Baku Light Gasoline treated by concentrated H_2SO_4	„	0·00	51·27	—	—	—	0·8
13	Ditto	„	10·05	42·66	8·61	1·167	0·00086	1·2
14	Ditto	„	20·03	34·16	17·11	1·171	0·00086	1·4
15	Cyclohexane	„	0·00	30·68	—	—	—	0·7
16	Ditto	„	10·15	21·65	9·03	1·124	0·00089	1·2
17	Ditto	„	10·16	21·58	9·10	1·116	0·00090	1·1
18	Ditto	„	20·18	13·02	17·66	1·143	0·00087	1·3
19	Ditto	„	20·17	12·96	17·72	1·138	0·00088	1·3

2. Aniline Method.

Benzene.—With the object of establishing the dependence of the value of the aniline co-efficient for benzene—from the aniline-point of the non-aromatic portion, there were prepared artificial mixtures of benzene and petroleum fractions (60–95° C. or 75–85° C.) derived from various crudes, with variable contents of naphthene hydrocarbons, previously freed from aromatic hydrocarbons. Cyclohexane with melting point of +4° C. was used as representing a maximum content of naphthene hydrocarbons. The results are given in Table I.

The co-efficients obtained from parallel experiments with solutions containing 10 per cent. of benzene deviate from the average value within ±0·003–0·004, and for 20 per cent. solutions—within ±0·001–0·002.

The value of the aniline co-efficient for benzene depends to a large extent on the aniline point of the non-aromatic portion—*i.e.*, with the lowering of the latter the co-efficient decreases accordingly.

The concentration of benzene also affects the co-efficient. The values of the co-efficient for the intermediate concentrations of benzene—namely, 5 per cent. and 15 per cent.—can be easily computed by interpolation.

Thus we obtained the following table in which the dependence of the aniline co-efficient for benzene on the above two factors is more clearly shown.

Table II.

Dependence of the Aniline Co-efficient of Benzene on the Concentration and on the Aniline-Point of the Non-Aromatic Portion.

Aniline-point of the non-aromatic portion, in ° C.	Co-efficients for different concentrations of benzene in per cent. by weight.			
	5	10	15	20
59·1	1·215	1·210	1·204	1·199
57·6	1·209	1·203	1·196	1·190
51·4	1·154	1·159	1·164	1·169
51·3	1·165	1·167	1·169	1·171
30·7	1·110	1·120	1·130	1·140

Fig. 1 shows graphically the relation of the change in the co-efficient to the aniline-point of the non-aromatic portion for benzene —contents of 5 per cent. and 15 per cent.

Separate aniline co-efficients, which were obtained experimentally, fit quite satisfactorily into the corresponding curves (Fig. 1). The average fluctuation of the co-efficients is ±0·002.

The curves of Fig. 1 served as a basis for preparing the following table of aniline co-efficients for benzene. (See Table III.)

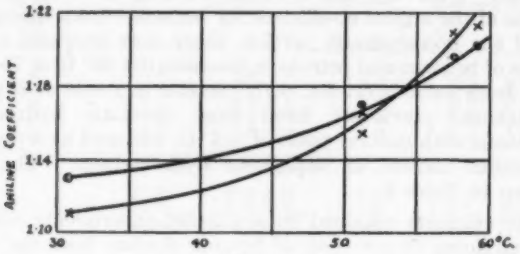


FIG. 1.

ANILINE-POINT OF THE NON-AROMATIC PORTION OF THE FRACTION.

It will be seen from the Table III that the co-efficient 1·15 as cited in the First Edition of "Standard Methods of Testing Petroleum and its Products," refers only to those cases where the aniline-point of the non-aromatic portion of the benzene fraction is contained within the limits of 47–51° C.

TABLE III.

Aniline Co-efficients for Benzene.

Aniline-point of the non-aromatic portion in ° C.	Co-efficient for benzene, when concentrated at:		Aniline-point of the non-aromatic portion in ° C.	Coefficient for benzene, when concentrated at:	
	0–10%	10–20%		0–10%	10–20%
60–59	1·23	1·21	53–51	1·16	1·17
59–58	1·22	1·20	51–47	1·15	1·16
58–57	1·21	1·20	47–43	1·14	1·15
57–56	1·20	1·19	43–39	1·13	1·14
56–55	1·19	1·19	39–35	1·12	1·14
55–54	1·18	1·18	35–31	1·11	1·13
54–53	1·17	1·18			

Toluene.—The aniline co-efficients for toluene, similarly to those for benzene, were obtained by means of preparing artificial mixtures of toluene with narrow fractions (95–122° C. or still narrower) derived from various crudes and freed from aromatics. These co-efficients are given in Table IV.

TABLE IV.

Aniline Co-efficients for Toluene.

Aniline-point of the non-aromatic portion in ° C.	Co-efficients for toluene, when concentrated at:		Aniline-point of the non-aromatic portion in ° C.	Co-efficients for toluene, when concentrated at:	
	0–10%	10–20%		0–10%	10–20%
61–60	1·26	1·24	50–48	1·20	1·19
60–58	1·25	1·24	48–46	1·19	1·19
58–56	1·24	1·23	46–44	1·18	1·18
56–54	1·23	1·22	44–42	1·17	1·18
54–52	1·22	1·21	42–40	1·16	1·17
52–50	1·21	1·20			

Xylene.—The so-called "Xylene-fraction" (122–150° C.) may comprise three isomeric xylenes and ethyl-benzol. The possibility of an accurate determination of the total quantity of aromatic hydrocarbons in the 122–150° fraction will depend on the extent of difference existing between individual co-efficients for each of the isomeric xylenes and ethyl-benzol.

In order to investigate this matter there were prepared 20 per cent. solutions of each of the four mentioned aromatic hydrocarbons in a refined 130–140° fraction of "Grozny" crude, and respective aniline-co-efficients were determined for each solution.

These co-efficients are given in Table V.

TABLE V.

Description of Hydrocarbon.	Aniline co-efficient.
Ethyl-benzol	1·30
Xylene (ortho)	1·26
Xylene (meta.)	1·28
Xylene (para.)	1·28

The aniline co-efficients fluctuate within a comparatively narrow range and the average value equals 1·28, which coincides with the aniline co-efficient for *m*-xylene (as well as para-xylene).

It is known, however,[7] that of all 3 isomeric xylenes in natural crude oils the largest proportion falls on *m*-xylene.

Therefore we have chosen *m*-xylene for the purpose of studying the dependence of the aniline-co-efficient for aromatics in the 122–150° C. fraction from the aniline-point of the non-aromatic portion.

[7] Dobriansky, "Analysis of Petroleum Products," page 243, 1925.

The co-efficients for *m*-xylene are given in Table VI.

TABLE VI.

Aniline Co-efficients for m-Xylene.

Aniline-point of the non-aromatic portion in ° C.	Co-efficients for *m*-xylene, when concentrated at :		Aniline-point of the non-aromatic portion in ° C.	Co-efficients for *m*-xylene, when concentrated at :	
	0–10%	10–20%		0–10%	10–20%
65–63	1·29	1·28	55–53	1·24	
63–61	1·28	1·27	53–51	1·23	
61–59	1·27		51–49	1·22	
59–57	1·26		49–47	1·21	1·22
57–55	1·25				

150–200° C. *Fraction.*—The exact determination of aromatic hydrocarbons in a 150–200° fraction represents a more difficult problem as compared with the previous cases, in view of a great variety of aromatic hydrocarbons having their boiling point within 150–200° C.

As an average representative of aromatic hydrocarbons of the above-named fraction a 170–175° C. cymol-fraction was taken, the cymol being obtained from Kalbaum and consisting, in accordance with its constants, mainly from para-cymol.

The aniline co-efficient for cymol is practically independent of the aniline point of the non-aromatic portion of a 150–200° C. fraction, and its average value is 1·57.

3. NITROBENZENE METHOD.

The nitrobenzene method for quantitative determination of benzene, toluene and xylene—exactly analogous with the aniline method—was recently introduced by Erskine.[8] The nitrobenzene co-efficients found by the latter are, respectively : 0·845 for benzene, 0·890 for toluene and 0·938 for xylene. As will be seen, further, the co-efficients found by us differ somewhat from those found by Erskine.

This difference should be attributed to the fact that the latter established his nitrobenzene points by using equal parts (by weight) of nitrobenzene and petroleum-fraction, whereas we determined the " maximum " nitrobenzene point—*i.e.*, the true critical solution temperature.

[8] *Oil and Gas Journal* page 144, August, 1926.

To represent the aromatic hydrocarbons of the 150–200° fraction cymol was used and the co-efficients were determined in the usual manner.

The nitrobenzene method, in view of the low temperature of nitrobenzene points, offers the best conditions in those cases where the proportion of aromatic hydrocarbons does not exceed 10 per cent. With a higher proportion of aromatic hydrocarbons, the nitrobenzene-points are rather too low and therefore less convenient for determination.

Therefore, in order to determine the co-efficients, we made artificial mixtures with only 10 per cent. contents of aromatic hydrocarbons.

The nitrobenzene co-efficients, calculated by us on the basis of experimental data, are given below in Table VII.

TABLE VII.

Nitrobenzene Co-efficients for Aromatic Hydrocarbons.

Description of aromatic hydrocarbon.	Nitrobenzene point of fraction after the extraction of aromatics, in ° C.	Co-efficient.
Benzene	11–10	1·02
„	10– 9	1·00
„	9– 8	0·98
„	8– 7	0·96
„	7– 6	0·95
Toluene	17–13	0·05
„	13– 9	1·04
m-Xylene	18–16	1·09
„	16–14	1·08
„	14–12	1·07
„	12–10	1·06
Cymol (150–200° C. frac.)	21–19	1·25
„ „ „	19–15	1·24
„ „ „	15–11	1·23

4. SPECIFIC GRAVITY METHOD.

The principal formulæ, which may be used for the purpose of calculating the percentage of aromatic hydrocarbons are as follows:—

(1) *For calculating the percentage of aromatics by weight.*

$$x = \frac{100\,D.(d_1 - d_2)}{(D - d_2)\,d_1} \quad .. \quad .. \quad .. \quad (1)$$

where: x = Percentage of aromatics by weight.
D = Specific gravity of aromatics only.
d_1 = Specific gravity of gasoline under test.
d_2 = Specific gravity of gasoline after extraction of aromatics.[9]

[9] Dobriansky, "Analysis of Petroleum Products," page 148, 1925. Zaborowsky's Method.

(2) *For calculating the percentage of aromatics by volume.*

$$y = \frac{100\,(d_1 - d_2)}{D - d_2} \quad .. \quad .. \quad .. \quad (2)$$

where: y = Percentage of aromatics by volume.
D = Specific gravity of aromatics only.
d_1 = Specific gravity of gasoline under test.
d_2 = Specific gravity of gasoline after extraction of aromatics.

(3) *For converting the percentage of aromatics by weight into percentage by volume.*

$$y = 100 - (100 - x)\frac{d_1}{d_2} \quad .. \quad .. \quad (3)$$

where: y = Percentage of aromatics by volume.
x = Percentage of aromatics by weight.
d_1 = Specific gravity of gasoline under test.
d_2 = Specific gravity of gasoline after extraction of aromatics.[10]

The results obtained through the application of the above formulæ are not strictly correct, due to the fact that in the process of mixing the aromatics with non-aromatic hydrocarbons a certain expansion of the mixture always takes place.

In order to obtain more accurate results Thole[11] advises to add the following corrections to the percentages of aromatics given by the formula (2).

TABLE VII.

Calculated percentage of benzene by volume.	Correction to be added in percentage by volume.	Calculated percentage of toluene by volume.	Correction to be added in percentage by volume.
5	0·3	5	0·2
10	0·6	10	0·4
15	0·8	15	0·6
20	1·0	20	0·7
25	1·2	25	0·9
30	1·3	30	1·0

However, the above corrections will only partially rectify the error, as they, in turn, depend to a considerable extent on the chemical composition of the non-aromatic portion, as will be seen from the data contained in Table VIII, arranged in accordance with experimental results obtained by us.

[10] "Standard Methods of Testing Petroleum and its Products," page 11, 1924, London.
[11] *Journ. Soc. Chem. Ind.*, 1929, **38**, 39T.

TABLE VIII.

Dependence of "Corrections" for the Calculated Percentage of Aromatics on the Chemical Composition of Non-Aromatic Portion.

Description of initial product.	Description of aromatic hydrocarbon.	Percentage of aromatic hydrocarbon by weight.	Percentage of aromatic hydrocarbons calculated by formula (1).	Correction in percentage by weight.
Hexhane (0·6624/23·1)	Benzene	25·11	24·35	+0·76
" "	"	51·56	49·81	+1·75
" "	"	75·16	74·08	+1·08
Cyclohexane.. ..	"	25·06	20·64	+4·42
"	"	50·16	44·81	+5·35
"	"	75·27	71·46	+3·81

The dependence of the correction being added—on the chemical composition of the non-aromatic portion—is very clearly expressed: in mixing aromatic hydrocarbons with paraffin hydrocarbons, these corrections assume their minimum values, whereas in mixing aromatics with naphthene hydrocarbons, the correction reach maximum values. Thus, when mixing together equal weights of benzene and hexane, the corresponding correction is ±1·75 per cent., but in mixing equal weights of benzene and cyclohexane, the correction will be as much as ±5·35 per cent.

Consequently, the only correct method is to determine, by means of preparing artificial mixtures of aromatic hydrocarbons with corresponding aromatic-free petroleum fractions having different specific gravities (*i.e.*, with different percentages of naphthene hydrocarbons), the functional relation between the specific gravity of the non-aromatic portion of fractions and the value of correction, or, which is more convenient in practice, the value of co-efficient similarly with the aniline and nitrobenzene methods.

The co-efficient is obtained, as was explained before, by dividing the percentage (by weight) of the aromatic hydrocarbon by the difference of specific gravities between a fraction mixed with the above aromatic hydrocarbon and a pure fraction.

In view of the fact that the co-efficient for the specific gravity method (as well as for the refractometric method) has values expressed in the order of thousands, and with the object of more convenient comparison of same with aniline or nitrobenzene co-efficients, we have conventionally divided the co-efficient as computed by 1000.

Therefore, in order to determine the percentage of aromatics, it will be necessary previously to multiply by 1000 the co-efficient $\left(\frac{k}{1000}\right)$ given in the following tables.

The determination of aromatics is done by means of the formula given earlier in this paper ($x=k.\ d$).

In this way we have determined the specific gravity co-efficients for toluene, *m*-xylene and cymol.

TABLE IX.

Specific Gravity Co-efficients for Benzene.

Specific gravity of non-aromatic portion at 15° C.	Co-efficients for benzene, when concentrated at :	
	0–10% by weight.	10–20% by weight.
0·695–0·697	0·71	0·70
0·697–0·699	0·72	0·70
0·699–0·701	0·72	0·71
0·701–0·703	0·73	0·72
0·703–0·705	0·74	0·73
0·705–0·707	0·75	0·74
0·707–0·709	0·76	0·74
0·709–0·711	0·77	0·75
0·711–0·713	0·78	0·76
0·713–0·715	0·79	0·77
0·715–0·717	0·80	0·78
0·717–0·719	0·81	0·79
0·719–0·721	0·82	0·80
0·721–0·723	0·83	0·81
0·723–0·725	0·84	0·82
0·725–0·727	0·85	0·83
0·727–0·729	0·86	0·84
0·729–0·731	0·87	0·86
0·731–0·733	0·88	0·87
0·733–0·735	0·90	0·88
0·735–0·737	0·91	0·89
0·737–0·739	0·93	0·91
0·739–0·741	0·94	0·92
0·741–0·743	0·95	0·93
0·743–0·745	0·96	0·94

In Table X are given the specific gravity co-efficients for toluene.

TABLE X.

Specific Gravity Co-efficients for Toluene.

Specific gravity of non-aromatic portion at 15° C.	Co-efficients for toluene, when concentrated at:	
	0–10% by weight.	10–20% by weight.
0·733–0·734	0·91	0·90
0·734–0·735	0·92	0·91
0·735–0·736	0·93	0·92
0·736–0·737	0·94	0·93
0·737–0·738	0·95	0·94
0·738–0·739	0·96	0·95
0·739–0·740	0·97	0·96
0·740–0·741	0·98	0·97
0·741–0·742	0·99	0·98
0·742–0·743	1·00	0·98
0·743–0·744	0·01	0·99
0·744–0·745	1·02	1·00
0·745–0·746	1·03	1·01
0·746–0·747	1·04	1·02
0·747–0·748	1·05	1·03
0·748–0·749	1·06	1·04
0·749–0·750	1·07	1·05
0·750–0·751	1·08	1·06
0·751–0·752	1·09	1·06
0·752–0·753	1·10	1·07
0·753–0·754	1·11	1·08
0·754–0·755	1·12	1·09
0·755–0·756	1·13	1·10
0·756–0·757	1·14	1·11
0·757–0·758	1·15	1·12
0·758–0·759	1·16	1·13
0·759–0·760	1·17	1·14

The influence of the isomeric nature of aromatic hydrocarbons of the 122–150° fraction upon the specific gravity co-efficient can be seen from the Table XI, where co-efficients are given for 20 per cent. solutions of isomeric xylenes and of ethyl-benzol in a 130–140° fraction free from aromatics.

TABLE XI.

Description of aromatic hydrocarbon	Co-efficient $\frac{k}{1000}$.
Ethyl-benzol	0·93
o-Xylene	0·88
m-Xylene	0·95
p-Xylene	1·02

The average value of co-efficients for the above four isomeric aromatic hydrocarbons=0·95, and coincides exactly with the co-efficient for *m*-xylene. Therefore, in further work, we have accepted *m*-xylene as average representative of aromatic hydrocarbons in the xylene fraction.

TABLE XII.

Specific Gravity Co-efficients for m-Xylene.

Specific gravity of non-aromatic portion at 15° C.	Co-efficients for *m*-Xylene, when concentrated at:	
	0–10% by weight.	10–20% by weight.
0·749–0·750	0·96	0·96
0·750–0·751	0·97	0·97
0·751.0·752	0·99	0·98
0·752–0·753	1·00	0·99
0·753–0·754	1·02	1·01
0·754–0·755	1·03	1·02
0·755–0·756	1·04	1·03
0·756–0·757	1·05	1·04
0·757–0·758	1·07	1·06
0·758–0·759	1·08	1·07
0·759–0·760	1·10	1·08
0·760–0·761	1·11	1·10
0·761–0·762	1·13	1·11
0·762.0·763	1·14	1·12
0·763–0·764	1·16	1·14
0·764–0·765	1·17	1·15
0·765 0·766	1·19	1·16
0·766–0·767	1·20	1·18
0·767–0·768	1·22	1·19
0·768–0·769	1·23	1·20
0·769–0·770	1·25	1·22
0·770–0·771	1·27	1·23
0·771–0·772	1·28	1·25
0·772–0·773	1·30	1·26
0·773–0·774	1·32	1·28
0·774–0·775	1·33	1·30
0·775–0·776	1·35	1·31
0·776–0·777	1·37	1·33

5. REFRACTOMETRIC METHOD.

The refractometric method is exactly analogous with the specific gravity method, which was discussed above. This method has been frequently used for the purpose of quantitative determination of individual aromatic hydrocarbons. Hoyte[12] proposed a refractometric method for the quantitative determination of the total

[12] *J. Inst. Petr. Techn.*, 1925, 11, 76–80.

quantity of aromatics in gasolines obtained by straight distillation. However, in the majority of cases, the chemical composition of the non-aromatic portion was not considered at all.

The refractive index co-efficients for benzene, toluene and *m*-xylene, obtained by us are shown in Tables XIII, XIV and XV.

TABLE XIII.

Refractive Index Co-efficients for Benzene.

Refractive index of non-aromatic portion at 15° C.	Refractive index co-efficients for benzene, concentrated at :	
	0–10%	10–20%
1·395–1·397	1·24	1·20
1·397–1·399	1·27	1·23
1·399–1·401	1·30	1·25
1·401–1·403	1·33	1·28
1·403–1·404	1·35	1·30
1·404–1·405	1·37	1·32
1·405–1·406	1·38	1·33
1·406–1·407	1·40	1·34
1·407–1·408	1·42	1·36
1·408–1·409	1·43	1·38
1·409–1·410	1·45	1·40
1·410–1·411	1·47	1·41
1·411–1·412	1·49	1·43
1·412–1·413	1·50	1·44
1·413–1·414	1·52	1·46
1·414–1·415	1·54	1·48

TABLE XIV.

Refractive Index Co-efficients for Toluene.

Refractive index of non-aromatic portion at 15° C.	Refractive index co-efficients for toluene, concentrated at :	
	0–10%	10–20%
1·408–1·410	1·48	1·42
1·410–1·412	1·50	1·44
1·412–1·414	1·52	1·46
1·414–1·416	1·54	1·48
1·416–1·417	1·56	1·50
1·417–1·418	1·59	1·52
1·418–1·419	1·60	1·54

TABLE XV.

Refractive Index Co-efficients for m-Xylene.

Refractive index of non-aromatic portion at 15° C.	Refractive index co-efficients for *m*-xylene, concentrated at:	
	0–10%	10–20%
1·417–1·419	1·53	1·49
1·419–1·421	1·55	1·53
1·421–1·423	1·58	1·56
1·423–1·425	1·62	1·60
1·425–1·427	1·65	1·63
1·427–1·429	1·70	1·65
1·429–1·431	1·75	1·68

6. CONTROL TEST CONSISTING OF PARALLEL DETERMINATION BY FOUR METHODS OF AROMATIC HYDROCARBONS IN GASOLINE DERIVED FROM A RUSSIAN (BIBI-EIBAT) CRUDE OIL.

In order to verify the system of quantitative determination of aromatic hydrocarbons evolved by us, a parallel determination of aromatics by means of the four described methods was made in a gasoline from a certain Russian Crude (Bibi-Eibat).

This gasoline was redistilled into fractions: 60–95° C., 95–122° C., 122–150° C., and 150–200° C., and for each fraction (except that boiling below 60°) the necessary constants were determined before and after the removal of aromatics. The removal of aromatics was effected by a twofold treatment with 98 per cent. sulphuric acid (shaking by hand with 3 volumes of acid for ¼ of an hour).

The results of the test are brought together in Table XVI.

In accordance with the data given in Table XVI, and by using the previously given tables of co-efficients for all four methods, the following quantities of aromatic hydrocarbons were found in each fraction. (See Table XVII.)

The data of Table XVII show a good convergency between the results of four methods. The variation between the percentages of aromatic hydrocarbons as determined by the aniline, nitrobenzene and specific gravity methods has an average value of ±0·13 per cent. for the first three fractions. The difference or results obtained by means of refractometric method, from the remaining methods, reaches, as could be expected, a somewhat greater figure, and the average value of variations constitutes ±0·3 per cent. As regards the aromatic hydrocarbons of 150–200° C. fraction, it will be seen that for these as well the aniline and nitrobenzene methods give closely convergent results.

TABLE XVI.

Description of fraction.	Aniline-point:		Variation of aniline point in ° C.	Nitrobenzene-point:		Depression of nitrobenzene point in ° C.	Specific at 15
	Before extraction of aromatics.	After extraction of aromatics.		Before extraction of aromatics.	After extraction of aromatics.		Before extraction of aromatics.
60–95° fraction .. (Benzene fraction)	51·36	53·12	1·76	5·39	7·80	2·41	0·7224
95–122° fraction .. (Toluene fraction)	51·33	54·31	2·98	4·76	8·11	3·35	0·7512
122–150° fraction .. (Xylene fraction)	53·74	58·26	4·52	4·32	9·75	5·43	0·7724
150–200° fraction ..	55·74	62·20	6·46	3·83	11·85	8·02	

TABLE XVI.

Nitrobenzene-point:		Depression of nitrobenzene point in ° C.	Specific gravity at 15° C.		Decrease of specific gravity.	
Before extraction of aromatics.	After extraction of aromatics.		Before extraction of aromatics.	After extraction of aromatics.		
5·39	7·80	2·41	0·7224	0·7203	0·0023	1·
4·76	8·11	3·35	0·7512	0·7477	0·0035	1·
4·32	9·75	5·43	0·7724	0·7674	0·0050	1·
3·83	11·85	8·02				

Decrease of specific gravity.	Refractive index			Variation of refractive index.
	Before extraction of aromatics.	After extraction of aromatics.	At 15° C.	
0·0023	1·3992	1·3980	22·7	0·0012
0·0035	1·4135	1·4113	22·3	0·0022
0·0050	1·4249	1·4210	22·8	0·0039

Percenta

Desc	
60–95°	
(Benz	
95–122°	
(Tolu	
122–150	
(Xyle	
150–200	

From
above
benzen
appear
determ
of eac

In c
are av
possibl
metho

The
by me
the de
less th
and su

In c
use (fo
metho
very li
nitrobe
be con
is suff

TABLE XVII.

Percentages of Aromatic Hydrocarbons in a Gasoline from Bibi-Eibat Crude Oil Determined by Means of Four Methods.

Description of fraction.	Percentages of aromatic hydrocarbons by weight, determined by means of methods:			
	Aniline.	Nitro-benzene.	Spec. grav.	Refracto-met.
60–95° fraction .. .. (Benzene fraction)	2·1	2·2	1·9	1·5
95–122° fraction .. .. (Toluene fraction)	3·7	3·5	3·7	3·3
122–150° fraction .. .. (Xylene fraction)	5·7	5·7	6·1	6·0
150–200° fraction	10·1	9·9		

7. GENERAL CONCLUSIONS.

From the comparison between the four methods described above we come to the following essential conclusions: For the benzene, toluene and xylene fractions, the refractometric method appears to be the simplest and the quickest. The process of determination requires very small quantities of products (2–3 c.c. of each fraction may suffice).

In cases where only small quantities of the gasoline to be tested are available, the refractometric method would be the only method possible. The error in the results given by the refractometric method is ±0·3 per cent.

The time required for the determination of the refractive index by means of Abbe's refractometer is about two minutes, whereas the determination of one aniline "maximum" point requires not less than fifteen minutes with a well-conducted testing equipment and sufficient operating skill.

In cases where greater accuracy is required it is advisable to use (for fractions with boiling point below 150°) the specific gravity method which, while possessing considerably greater simplicity, is very little or hardly at all inferior in accuracy to the aniline and nitrobenzene methods. The determination of specific gravity can be conducted by means of Westphal's balance, provided the latter is sufficiently sensitive and the operation itself is conducted in a

large diameter cylinder (with not less than 70 or 80 c.c. of liquid). In the remaining cases a pyknometer should be used.

The determination of aromatic hydrocarbons in the 150–200° fraction should be effected by means of either the aniline or the nitrobenzene method. The variable composition and structure of aromatic hydrocarbons in the 150–200° C. fraction do not affect the critical solution temperature so much as they do the specific gravity or the refractive index. Consequently, the determination of aromatic hydrocarbons in the 150–200° C. fraction by means of the last two methods is liable to give excessive errors. The above consideration applies in a still greater degree to the determination of aromatic hydrocarbons in kerosines, where, in addition to the different structure of the side chains, there is a different structure of the nucleus—*i.e.*, benzene or naphthalene.

Thus it is clear that the specific gravity and refractometric methods can be successfully applied only to fractions boiling below 150° C.

Comparing the aniline and nitrobenzene methods to each other, we would in many cases give preference to the nitrobenzene method which possesses the following advantages as compared with the aniline method :—

1. Lower critical solution temperatures and therefore more rapid determination.

2. Lesser fluctuations of nitrobenzene co-efficients due to variation of chemical composition of the non-aromatic portion.

3. Greater stability of nitrobenzene.

In order to accelerate the determination of the maximum aniline or nitrobenzene point, one must bear in mind that the volume-

TABLE XVIII.

Limits of boiling temperatures of fraction.	Volume ratios of aniline to petroleum product required for maximum-point, at the following percentages of aromatics by weight:		
	0%	10%	20%
60–95°	0·8–0·9	1·2	1·3–1·4
95–122°	0·9	1·3	1·5
122–150°	1·0	1·2–1·3	1·4–1·6
150–200°	1·0	1·4	1·6

ratios of aniline and a given-petroleum-product depend largely on the percentage of aromatics: the higher the percentage of aromatics the larger quantity of aniline shall be required to obtain the maximum point. This will be seen from the Table XVIII.

An analogous correlation of the above factors exists also for the nitrobenzene method.

To determine the maximum point for gasoline-fractions separated from aromatics it is necessary to use 0·6–0·7 of a volume per 1 volume of fraction, and for gasoline-fractions containing 10 per cent. of aromatics 0·9 to 1 volume.

The boiling temperature of fraction has no appreciable influence.

Recent Development in the Art of Cracking in the Vapour Phase.*

By C. R. Wagner.

During the last few years fresh impetus has been given to the development of methods for the conversion of heavy petroleum hydrocarbons into lighter fractions suitable for use in internal combustion engines. This development has been largely along the lines of cracking in the Vapour Phase, just as ten years ago there occurred a vigorous exploitation of methods for cracking in the Liquid Phase. At that time the need was for greater production of motor spirit; the world's output of crude oil was not keeping pace with the rapidly increasing numbers of motor cars, and its exhaustion within a short time was confidently predicted. At that time, also, the general demand was for a petrol as nearly as possible akin to the straight-run spirit obtained from crude oil, and no worse stigma could be attached to motor spirit than to brand it as "cracked."

The situation at the present time is different. There is a general demand for cracked petrol, owing to its higher anti-knock value, this change in attitude having been brought about by the development of the high compression automobile engine. These engines have grown very popular because of their power, quick pick-up and general high efficiency under varied conditions. Such engines knock severely when using most unblended straight-run spirits or liquid-phase cracked-spirit obtained from paraffin-base oils. Such detonation is not only unpleasant to hear but is hard on the engine, which under detonating conditions does not deliver its maximum power or give good acceleration. The refiner was, therefore, compelled to have recourse to one of several methods in order to raise the Highest Useful Compression Ratio of his product.

The first and most obvious way was to crack, in equipment of then existing type, selected charging stocks capable of giving a product of a high anti-knock rating. The supply of such raw material is limited, and this method, therefore, only available to a few. A second method adapted for the amelioration of low grade spirit was the use of "dopes," and there is no doubt that the wide distribution of such fuels has been largely instrumental in making the present-day automobile engine a possibility. Many refiners, however, were not able to adopt such a course and turned to the use of low end-point gasoline obtained from natural gas. This is a valuable method and has led to the wide distribution of such

*Based upon a paper read before the National Petroleum Association at Cambridge Springs, Pennsylvania, on April 25, 1929.

blended spirits, but all of these methods have considerable disadvantages, and there has been an unceasing search for genuine hydrocarbon motor spirit of ordinary boiling range capable of replacing "doped" petrols. It is for this reason that so much attention has been paid to the possibilities of Vapour Phase cracking, the product from which has been recognised for a long time as being of particularly high anti-knock value.

Early History.

To those who have thought of cracking as being accidentally discovered in 1861 by a careless stillman, it will be of interest to learn that Dalton in 1809 conducted an extensive series of experiments on the decomposition of hydrocarbon vapours by means of electric sparks.

Sixteen years later Faraday worked on the same problem and isolated benzene and several of the unsaturated hydrocarbons. In 1855 Professor Silliman made "oil gas" from petroleum hydrocarbons by high temperature cracking. His classic researches indicated many of the possibilities of petroleum chemistry, the realisation of which in practice was not effected until comparatively recent times. Berthelot's work on the decomposition of petroleum at high temperatures was published prior to 1870, and Thorpe and Young began their work at least as early as 1865. In those early days, however, the demand was for lamp oil and not the light motor fuel fractions required to-day. In 1862 we find Breitenlohner winning a grand prize at the London Industrial Exposition for such a product produced by a high temperature vapour phase cracking process.

In the shortage of coal tar products which followed upon the early stages of the development of the dyestuff industry Nikiforoff found an incentive to develop his processes for the manufacture of aromatic hydrocarbons from petroleum. The growth of the coal tar industry, however, relegated this process and others of a similar nature to the scrap heap, though they have an important place in the history of the development of the cracking industry.

It appears that Cowper-Coles in 1906 was the first person to design and operate a cracking process for the production of light motor fuel. He passed heavy vapours through small metal tubes heated to high temperatures, and then condensed the cracked vapours, and he appears to have noted some of the problems in vapour phase cracking which evidently escaped later investigators. Noad, Sabatier, Testelin and Renard, Laing, Greenstreet, Lamplough, Turner, Hall and others rapidly followed the lead of Cowper-Coles, all of them strangely enough working in the vapour phase.

The development of the Burton process of liquid phase cracking by the Standard Oil Company (Indiana), for the manufacture of motor fuel abruptly changed the course of events in this field. Hall's process in England and Rittman's in America were able to make some headway during the war, but the return to peace caused their abandonment.

Examination of these processes and their operating conditions reveal several reasons for their failure. Perhaps the greatest stumbling block from the operating standpoint was coke formation. Tubes would plug up and burn out, towers and traps filled with carbon and had to be torn down for cleansing. Some of the inventors—*e.g.*, W. A. Hall—provided a packed tower to facilitate the separation of this carbon and its ready removal from the system. The writer once saw a 10-inch vapour line plugged in this manner after 24 hours of operation so solidly that it had to be torn down and scrapped. Altogether, aside from the inconveniences thus caused—and continuity of operation was out of the question—there was a very great hazard to life and property. This was particularly true in some of the systems where super-atmospheric pressures were used. Carbon forming on the walls of highly heated tubes or chambers acted as an efficient insulator and allowed the steel to become heated above its softening point.

The pressure on the system then caused a rupture at the point where the coke had deposited, the damage done being more or less dependent upon the location of the hot spot and the quantity of oil vapour in the system. All methods seemed to fail in the attempt to prevent the formation of this deposit and the consequent interruption of operation, and it is only within the last few years that any success has attended these efforts.

Aside from the difficulty encountered with carbon formation, attempts to crack in the vapour phase appeared doomed to failure because of excessive gas formation. In nearly every case for each gallon of motor fuel distillate produced a gallon of gas oil was converted into fixed gas and coke. As recently as 1926 a well-informed technical expert, with years of experience in vapour phase cracking, informed the writer that one must expect from a single throughput no more than 25 per cent. motor fuel, 25 per cent. gas, and 50 per cent. light fuel oil. This light fuel oil could be recycled, but in his estimation was scarcely worth it. It is small wonder that the oil industry looked askance at such processes, which could only be economical if the product were to receive a very large premium over ordinary spirit. The size of this premium is already well established by the prices of current premium motor fuels, and in few instances in America does it exceed three or four cents per gallon. Unless its sale were possible, the disposal of such

quantities of gas would also be a tremendous problem. The proportions given above indicate that 90 to 100 cubic feet of gas would be produced for each gallon of motor fuel made.

A third objection to vapour phase cracking was the high consumption of fuel. Vapour temperatures of 1100 degrees Fahrenheit meant stack temperatures well over 1000 degrees Fahrenheit under the best of conditions, and 1500 degrees Fahrenheit was not unusual. Excessive furnace temperatures increased coke formation, and failure to use the radiant heat from the combustion chamber forced fuel costs still higher. The use of excess air to keep flame temperatures down caused such rapid oxidation of tubes that their life became a matter of days, or even hours.

If anyone were brave enough to face these three formidable antagonists, a fourth usually disposed of him forthwith—viz., treatment of the raw distillate so as to produce a satisfactory motor fuel. This distillate seemed to have everything wrong with it that any petroleum distillate was ever accused of. It was yellow, and seemingly averse to becoming water white; it had a very bad odour and it accumulated gum rapidly. It did not respond in the usual manner to treatment with acid, as many refiners can attest. One reported treating a thousand barrels of such distillate in an open agitator with five pounds per barrel of 66 degrees Baume acid. The oil temperature rose from 70 degrees Fahrenheit to 180 degrees Fahrenheit, and the final recovery of motor fuel was about 60 per cent. Of course, a large part of this loss was polymerisation loss, but the evaporation was heavy enough to make that part of the plant a considerable fire hazard for hours.

In spite of all these disadvantages, however, the finished motor fuel gave most remarkable performances in the new high compression engines. It could be blended with straight-run gasoline in equal proportions, and the blend was as good or better than the 40 per cent. benzol blends on the market. This blend gave smooth acceleration, unusual power, more mileage, less detonation, and less carbon than most of the doped fuels or so-called premium gasolines on the market. It is therefore not surprising that the popularity of these high compression engines caused a revival of interest in vapour phase cracking. It appeared possible to get an ideal motor fuel in this way, if the difficulties outlined above could be overcome.

Of the methods available to-day for cracking in the vapour phase, the "Gyro" process has not only overcome the difficulties outlined above but has reached the stage of having five plants operating and four more with construction well under way. The capacity of these nine plants is 15,000 barrels of "gas oil" per diem. Descriptions of the process have already been given in the technical

press[1], but the following résumé of the methods adopted may conveniently be given :—

The charging stock is delivered in the form of spray into the hot vapours leaving the converter, the residue and any condensed vapours passing to a hot oil reservoir which acts as a collector for all oil entering the system which has not been transformed into motor spirit, fuel oil or gas. At a regulated rate of flow this hot oil is passed to an "economiser" in such quantity as will supply the correct quantity of vapour to the converter, this excess being returned through heat exchangers to the charging stock tank. The heated oil is passed through an evaporator to drop out non-volatile material and the vapour thence to a separator for the removal of entrained liquid. The cleaned vapours are distributed through the tubes of the converter in parallel, the tubes being fitted with catalytic cores. Superheated steam is introduced into the system through the evaporator in quantity not exceeding 3 per cent. by weight of the vapours. The cracking plant proper is linked up with modern fractionating and gas recovery plant.

Commercial operation of Vapour Phase cracking on these lines followed rapidly on the discovery of the causes of the troubles detailed above. Briefly, it was found that carbon formation was almost entirely due to the use of excessive local temperatures or to insufficient control of the cracking reaction. The essential feature is good heat transference, and when this is attended to and the actual time of reaction regulated to conform to determined limits, carbon formation is practically nil. Thirty-day runs are common occurrences on the operating units of to-day, and even then shut down is most often a matter of general plant convenience, and it is doubtful whether at the end of such a run 100 lb of carbon could be collected from all parts of the plant. It may be taken, therefore, that carbon or coke formation has definitely been liminated.

Excessive gas production has been found to be due partly to lack of control of the flow of vapours in the reaction zone and failure to regulate the temperature of reaction sufficiently closely. A variation of 5° F. in the temperature of reaction, other conditions remaining constant, causes a wide fluctuation in the proportion between fixed gas and motor spirit. Changes in the character of the material to be cracked have less influence than the factors of heat transference, flow and temperature control, and have much less effect than in the case of liquid phase cracking. It should be realised, too, that although the actual volume of gas production is still twice that made by liquid phase processes, the

[1] Wagner, *Oil and Gas Journal*, April, 1929; Auld, *Petroleum Times*, January, 1929.

extra gas is really made at the expense of residue or fuel oil production and not by reducing the yield of motor fuel distillate.

In practice, considerable heat economies have been effected by modern methods of plant erection and by taking advantage of the special features of vapour phase operation. Such matters have been dealt with elsewhere.[2]

Refining the Distillate.

The problem of refining vapour phase cracked spirit has always been recognised as a difficult one, owing to the unsaturated nature of the product. Even after the spirit has been refined to a point where it meets all engine requirements as a motor car fuel, further difficulties have stood in the way owing to the arbitrary standards set up on behalf of the consumer in the days of straight-run petrol. These difficulties have now been overcome. The smell, for example, though distinct from straight-run spirit, is pleasant and quite different from that of the old-fashioned cracked spirit of the earlier vapour phase processes.

The colour problem has also been solved. Due to the highly unsaturated character of the hydrocarbons present, it has not been an easy matter to work out a method of removing colouring matter without at the same time removing a large percentage of the desirable compounds possessing high anti-knock value. At the present time, however, several methods are available for this purpose, some involving new equipment, others merely adaptations of existing methods. It can now be safely stated that methods are available which will yield at least 95 per cent. of highly satisfactory motor fuel of good smell and water white colour from endpoint vapour phase cracked distillate.

Any gasoline or motor fuel containing olefines, on standing exposed to the air, forms gum. The rate at which this gum forms is dependent upon the time of such exposure, the concentration of the oxygen in the atmosphere over the liquid, the percentage and kind of olefines, the temperature, the amount of agitation and the extent to which actinic light or other catalyzing influences may have access. In this paper it is not possible to go into great detail on this important phase of the refining of vapour phase cracked distillate, but certain points require brief treatment.

Since this distillate contains 50 per cent. or more of olefines, it is evident that gums will accumulate in it on standing in storage. The olefines cannot be wholly removed by treatment with acid for obvious economical reasons, nor can they be converted into saturated hydrocarbons by hydrogenation without losing the anti-

[2] Wagner, *loc. cit.*

knock quality of the product. It has been found possible, however, to produce spirit which is entirely gum free when first made, and while in this condition to give it a treatment which inhibits subsequent gum formation even under somewhat severe conditions. For example, a sample of vapour phase spirit thus treated was blanketed with an atmosphere of pure oxygen in a clear glass bottle and set in a north window. Another sample, not treated, was set beside it. At the end of 35 days the untreated sample showed 0·0447 grams of gum, whereas the treated sample contained only 0·0064 grams.

It is noteworthy that refiners generally are alive to the faults of the old copper dish method of determining gum in motor fuels. Aside from the difficulty encountered in getting check determinations, it does not give even an indication of the amount of preformed gum present. The copper dish acts as a catalyzer, and the large volume of fuel to be evaporated requires such a long time for the test that most of the gum found has been formed during the test. The wide variation in results obtained makes the method of little value even in estimating the stability of a fuel.

An excellent paper on the effect of gum upon engine performance is that of Voorhees and Eisinger, of the Standard Oil Company of Indiana.[1] The authors show very clearly that it is only preformed gum that affects engine performance, a statement borne out by the results of marketing millions of gallons of vapour phase cracked motor fuel during the past three years. They recommend the method of Smith and Cooke[2] for the determination of preformed gum, in which 20 c.c. are evaporated from a 30 c.c. pyrex dish of special shape in an atmosphere of steam. With very slight modefications this method has been in use for nearly three years in half a dozen laboratories widely separated, and is giving very satisfactory results. An equally satisfactory method for determining potential gum has not yet been found.

The characteristics of the products of vapour phase cracking are worthy of more attention than can be given them here. The motor fuel produced contains no more than traces of paraffins, and these are all under the hexanes in size. When analysed by the method of Egloff and Morrell it shows 45 to 50 per cent. olefines, 40 to 45 per cent. aromatics, and the balance naphthenes, with paraffins wholly absent. It is known that the dry gas contains less than 0·5 per cent. of butane and isobutane; hence it seems reasonable to expect only very small quantities of the higher paraffins to be present in the motor fuel. The specific gravity of the motor

[1] Read before the ninth annual meeting of the American Petroleum Institute at Chicago, December 7th, 1928.

[2] Bureau of Mines Report, Serial No. 2394 (1922), Bureau of Mines Report, Serial No. 2686 (1925).

fuel made from a Pennsylvania gas oil runs about 0·03 higher than the straight-run product of the same distillation range.

When the operation is such as to produce the optimum quantity of distillate the finished motor fuel, apparently without regard to the character of the charging stock, has a uniformly high anti-knock value. It should be pointed out that no automobile engine on the market to-day has a high enough compression ratio to warrant the use of a fuel having an anti-knock rating higher than 40 to 45 per cent. of benzol. By blending equal volumes of straight-run gasoline and vapour phase cracked motor fuel there is produced a fuel having an anti-knock rating of 40 to 45 per cent. benzol. Expressed in other words, vapour phase cracked motor fuel has a blending value of 80 to 90 per cent. of the value of motor benzol. Thousands of tests on a laboratory engine and many demonstrations with 4-, 6- and 8-cylinder automobiles have demonstrated this statement beyond question.

The distillation range of the finished motor fuel is somewhat different from ordinary gasoline, being richer in the lower boiling fractions. This makes it unnecessary to add natural gas gasoline, as must usually be done with liquid phase cracked fuel, and therefore increases its value as a blending agent. Partly due to this greater volatility, but more particularly because of its aromatic character, vapour phase cracked spirit has a lower viscosity than ordinary petrol. Its freezing-point is considerably below minus 100° F., a point of considerable value in making an aviation fuel.

A very remarkable fact, especially in view of the importance of West Texas and Venezuela production, is the relatively low sulphur content of vapour phase cracked distillate. Two examples may be quoted. In one a light recycle stock from a liquid phase cracking operation was charged to a vapour phase plant. This recycle oil contained 0·80 per cent. sulphur, but the vapour phase cracked distillate contained only 0·13 per cent. sulphur. In the other instance a Mexican gas oil containing 1·20 per cent. sulphur was cracked in the vapour phase, and there was found in the distillate only 0·23 per cent. sulphur. From these facts it appears that marketable motor fuel may be made from highly sulphurous crude oils more easily by vapour phase cracking than can be done with liquid phase equipment. The gas, of course, is correspondingly richer in hydrogen sulphide, since the sulphur seems to be split off in this form.

Fixed Gases.

The fixed gas produced after removal of the motor fuel content has a specific gravity of about 1·0 and a fuel value of approximately 1700 B.TH.U. per cubic foot. Its composition varies little except for the H_2S content, which depends upon the sulphur content of

the charging stock. The average analysis of the gas from Pennsylvania gas oil is as follows :—

	Per cent.
CO_2+H_2S	0·25
CO	0·15
H_2	7·00
C_2H_4	27·00
C_3H_6	16·00
C_4H_8	9·00
C_5H_{10}	1·00
Saturated hydrocarbons	39·60

It can readily be seen that this gas has excellent possibilities in the field of gas manufacture where it can be substituted for " oil gas " as an enriching agent. Plants not immediately in the vicinity of a water gas or producer gas plant could very easily liquefy the propylene-butylene fraction and ship it by tank car for such purposes, utilising the residues for plant fuel.

The most inviting possibilities for the gas lie, however, in the field of chemical manufacture. One chemical concern in America already uses large quantities of it for its ethylene content. The uses for ethylene are many, and indications point to a steadily increasing demand. A few of the products that may be manufactured from it are acetic acid, ethyl alcohol, ethylene dichloride, ethylene glycol, pure ethylene for anæsthesia, and mustard gas. Propylene, which can be recovered in a state of high purity, can be used as a refrigerant, or may be used in the preparation of isopropyl alcohol, isopropyl acetate, acetone, and propylene glycol.

It is not known as yet in what proportions the three butenes are found, though all are present. This fraction may be used in the preparation of isobutyl and tertiary butyl alcohols, butyl acetates for cellulose acetate solvent, and methyl ethyl ketone. It is understood that some effort has been made to use the butadiene in making synthetic rubber, but the concentration is rather low for this purpose. It is possible that its synthesis through the isopropyl alcohol fraction might be feasible in case rubber prices became high enough. At present, however, that possibility seems remote.

The vast quantities of raw materials which will be made available for chemical synthesis in this manner may be realised when present production is considered. From a daily throughput of 4,000 bbls. of gas oil nearly 5,000,000 cubic feet of dry gas are produced. This means 1,350,000 cubic feet of ethylene, 800,000 cubic feet of propylene, and 450,000 cubic feet of the three butenes.

A third use for this gas, which bids fair to consume the major portion of its unsaturated hydrocarbon content, is in the synthesis of motor fuel. Preliminary experiments along this line indicate that a very highly anti-knock product especially suited for aviation motor fuel can be made from it in large quantities at low cost. It is hoped that a more detailed report on this feature will be available later.

REVIEWS.

PETROLEUM DEVELOPMENT AND TECHNOLOGY, 1928-29. American Institute of Mining and Metallurgical Engineers. New York, 1929. Pp. 623. $5 net.

This is the fourth volume of the annual series issued by the Petroleum Division of the Institute and is divided into eight chapters covering Production Engineering, Petroleum Research, Petroleum Production—United States and Foreign, Petroleum Economics, Petroleum Engineering Education, Petroleum Refining, Gas Transportation.

The chapter on Production Engineering occupies half of the book and the subjects dealt with include crooked holes, pumping, well spacing, pressure control, gas-oil ratio, re-pressuring, gas-lift, and concludes with a lengthy paper on the manufacture and use of nitro-glycerine.

The Petroleum Research chapter deals chiefly with investigations regarding oil production, while statistics and details of conditions prevailing in the principal oil-producing countries of the world are to be found in the chapter on Production. Such topics as over-production, supply and demand and the market price of oil securities are discussed under Economics.

The total number of individual papers included in the work is fifty, together with their discussions, and the book forms a useful source of information regarding up-to-date methods and conditions and should prove of value to the petroleum technologist. GEORGE SELL.

DIE VERWASSERUNG VON ERDOLFELDERN, IHRE URSACHEN UND BEKAMPFUNG. By Dr. Walter Kauenhowen. Berlin: Verlag von Julius Springer, 1928. Pp. 80+vi.

This little pamphlet deals essentially with problems concerned with water in oilfields, in particular the causes, effects and control of what has been termed the "watering" of oil-pools. The subject is by no means new; neither can it be said that the author presents it in any novel guise. But oilfield hydrology, especially in its practical aspects, has steadily come to assume such a vital factor in economic developments, it is so much an integral part of modern petroleum production engineering, that all contributions to the subject, especially those presenting other than British and American ideas, which are to a large extent stereotyped, are welcome.

As might be expected from a German text, the subject is here treated very systematically, under a number of headings and sub-headings which show at a glance the principal facts discussed and, incidentally, facilitate both reference and reading. There are also numerous illustrations, many of them, however, familiar from American and other technical literature.

The author first deals with the possible extent of water-flooding of oil-pools and the damage caused thereby, and quotes examples from Germany, Poland, Mexico and the United States. He then passes to a general consideration of hydrological conditions in oilfields, embracing among other things, salt-water encroachment, separation of different waters, oil and water mixing, and data of chemical constitution of waters, also methods of expressing and interpreting analyses. This chemical section is weak, largely because it is very brief and not as up to date as it might be.

The next section on the causes of oilfield-watering is good, though the author does not seem to get far beyond his various references, as is apparent at once from some of the text figures. Among the important causes discussed are included faulty shut-off (as regards position in the well), defective casing

or water-string, corroded or damaged casing, bad drilling, the effects of drilling too deep into oil-sands and the possibilities of bottom water thus trapping oil, edge-water advance due to excessive development in one part of the field, disregard for fundamental principles of production, etc. He then proceeds to a discussion of methods of controlling water-movements, and this is undoubtedly the best part of his essay. Practically all the well-known devices are described, the use of various packers, and especially the technique of cementation, being made clear both in text and diagram.

The book concludes with appendices which exemplify, *inter alia*, some of the varied regulations for water-control in oilfields of different countries. It is a little difficult to understand the purpose of these quotations, unless it be to impress on the reader the necessity of adequate official control of drilling to prevent oilfield-watering, such as exists in California, for example. The author's choice of actual cases in this connection would have been more valuable had he taken more recent data. The bibliography is short but adequate to a book of this size.

H. B. MILNER.

ANORGANISCHE UND ORGANISCHE ENTFARBUNGSMITTEL. Leopold Singer. Steinkopff, Leipsig, 1929. Rm. 20.

There is no better way of assisting in the propagation of knowledge than by systematically and carefully compiling all known data on a particular subject in the form of a monograph.

The well-known publishing firm of Steinkopff, of Leipsig, has within the last few years undertaken the production of a number of such monographs concerned with the Chemical Industry, and the issue before us by the eminent Viennese Technologist, Dr. Leopold Singer, is a worthy addition to the series.

This monograph is the twentieth volume produced under the auspices of Dr. Ressow, and is entitled "Anorganische und Organische Entfarbungsmittell." It is concerned with the description, preparation and properties of a wide range of decolorising materials, both organic and inorganic. The various sections of the book are as follows:—

The Properties of Natural Bleaching Earths, such as bentonite, silica, bauxite and various gels, decolorising carbons and activated charcoals; The Theoretical Problems concerned with Absorption in Mineral Oil Refining; The Preparation of Bleaching Materials, including a full analysis of the Patent Literature. This section deals with the technical production of various proprietary earths, silica gel, ferric oxide, titania gel and special charcoals.

A section follows that is concerned with the application of these materials to the decolorising of vegetable and mineral oils, petroleum and sugar.

There is an excellent index, both of authors and subjects, and a patent register that will be found of the utmost value.

Altogether the volume is one that is essential to the Petroleum Technologist.

A. E. DUNSTAN.

THE REACTIVITY OF COKE. 2. THE EXAMINATION OF A NUMBER OF METALLURGICAL COKES. By J. H. Jones, J. G. King and F. S. Sinnatt. Fuel Research Technical Paper No. 22. London: H.M. Stationery Office. Pp. vi. + 30, with 15 figs. 1s. net.

It is shown that a broad correlation exists between the behaviour of coke in the "reactivity" apparatus, described in Fuel Research Technical Paper No. 18, and its physical strength as indicated by the shatter test. Indications are also given of the effect of carbonising conditions and of certain inorganic constituents.

ects of
r thus
e part
. He
ments,
e well-
lly the
n.
ome of
ntries.
unless
trol of
ample.
n more
rt but
NER.

Singer.

e than
ticular

in the
graphs
minent
series.
ices of
bunga-
perties
. The

silica,
rcoals;
fining;
of the
various
rcoals.
terials
r.
patent

echno-

TAN.

METAL-
Fuel
Office.

f coke
Paper
Indica-
certain